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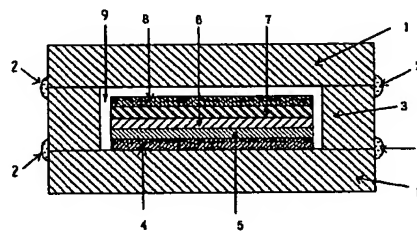
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(54)【発明の名称】 有機エレクトロルミネッセンス素子とその製造方法

(57)【要約】 (修正有)

【構成】 少なくとも一方が透明または半透明である一対の陽極および陰極からなる電極間に、少なくとも発光層を有する有機エレクトロルミネッセンス素子において、該発光層が固体状態で蛍光を有する高分子蛍光体を含み、陽極表面からの間隔または陰極表面からの間隔が1 μ m以上2 mm以下である2枚の透明または半透明の板またはフィルムにより挟まれ、かつ外気と接触しないように隔絶されてなり、該素子と該板またはフィルムとの間の空間は不活性な気体で満たされてなる有機エレクトロルミネッセンス素子。

【効果】 高輝度、高発光効率、低駆動電圧の有機EL素子で、長期の保存においてもダークスポットがほとんど生成および成長しない。



【特許請求の範囲】

【請求項1】 少なくとも一方が透明または半透明である一対の陽極および陰極からなる電極間に、少なくとも発光層を有する有機エレクトロルミネッセンス素子において、該発光層が固体状態で蛍光を有する高分子蛍光体を含み、該高分子蛍光体は、一般式(1)で示される繰返し単位を全繰返し単位の50モル%以上含み、ポリスチレン換算の数平均分子量が $10^3 \sim 10^7$ であり、該有機エレクトロルミネッセンス素子が、陽極表面からの間隔または陰極表面からの間隔が $1\mu\text{m}$ 以上 2mm 以下である2枚の透明または半透明の板またはフィルムにより挟まれ、かつ外気と接触しないように隔絶されてなり、該素子と該板またはフィルムとの間の空間は不活性な気体で満たされてなることを特徴とする有機エレクトロルミネッセンス素子。



(ここで、Arは、共役結合に関与する炭素原子数が4個以上20個以下からなるアリーレン基または複素環化合物基であり、R、R'はそれぞれ独立に水素、炭素数1~20のアルキル基、炭素数6~20のアリール基、炭素数4~20の複素環化合物、シアノ基からなる群から選ばれる基を示す。)

【請求項2】 不活性な気体が、窒素、アルゴン、ヘリウムまたは二酸化炭素であることを特徴とする請求項1記載の有機エレクトロルミネッセンス素子。

【請求項3】 板またはフィルムが、陽極または陰極の基板であることを特徴とする請求項1記載の有機エレクトロルミネッセンス素子。

【請求項4】 不活性な気体中で、透明または半透明な板またはフィルム上に作製した有機エレクトロルミネッセンス素子を囲むように、透明または半透明な板またはフィルム上に $1\mu\text{m}$ 以上 2mm 以下のスペーサーを置き、この上から別の透明または半透明な板またはフィルムをのせ、スペーサーと2枚のそれぞれの透明または半透明な板またはフィルムとの接合部を光硬化型または熱硬化型接着剤で接合し、該接合部を光硬化または熱硬化させ、2枚の透明または半透明な板またはフィルムを接合することを特徴とする請求項1記載の有機エレクトロルミネッセンス素子の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、高分子蛍光体を用いた有機エレクトロルミネッセンス素子（以下、有機EL素子とすることがある。）とその製造方法に関する。

【0002】

【従来の技術】 無機蛍光体を発光材料として用いた無機エレクトロルミネッセンス素子（以下、無機EL素子とすることがある。）は、例えばバックライトとしての面状光源やフラットパネルディスプレイ等の表示装置に用いられているが発光させるのに高電圧の交流が必要であ

った。近年、Tangらは有機蛍光色素を発光層とし、これと電子写真の感光体等に用いられている有機電荷輸送化合物とを積層した二層構造を有する有機EL素子を作製した（特開昭59-194393号公報）。有機EL素子は、無機EL素子に比べ、低電圧駆動、高輝度に加えて多数の色の発光が容易に得られるという特徴があることから素子構造や有機蛍光色素、有機電荷輸送化合物について多くの試みが報告されている（ジャパニーズ・ジャーナル・オブ・アプライド・フィジックス（Jpn. J. Appl. Phys.）第27巻、L269頁（1988年）、ジャーナル・オブ・アプライド・フィジックス（J. Appl. Phys.）第65巻、3610頁（1989年））。

【0003】 これまでに、発光層に用いる材料としては、低分子量の有機蛍光色素が一般に用いられており、高分子量の発光材料としては、WO9013148号公開明細書、特開平3-244630号公報、アプライド・フィジックス・レターズ（Appl. Phys. Lett.）第58巻、1982頁（1991年）などで提案されていた。WO9013148号公開明細書の実施例には、可溶性前駆体を電極上に成膜し、熱処理を行なうことにより共役系高分子に変換されたポリ（p-フェニレンビニレン）薄膜が得られ、それを用いたEL素子が開示されている。また、特開平3-244630号公報には、それ自身が溶媒に可溶であり、熱処理が不要であるという特徴を有する共役系高分子が例示されている。アプライド・フィジックス・レターズ（Appl. Phys. Lett.）第58巻、1982頁（1991年）にも溶媒に可溶な高分子発光材料およびそれを用いて作成した有機EL素子が記載されている。しかし、これらの材料を用いて作成された有機EL素子は、発光効率が必ずしも十分に高くはなく、保存中にダークスポットと呼ばれる輝度の低い欠陥が発光面に生じ、表示品位を低下させていた。

【0004】 低分子の有機蛍光色素を用いた有機EL素子については、陰極の金属材料に保護層としてインジウム、アルミキノリノール鉛体等の単独材料または共蒸着された固体材料や、シリコンオイルや弗素化炭素などの液体材料を電極の保護層として用いた有機EL素子が特開平5-101892、159881、129080、41281号公報に開示されている。

【0005】 しかしながら、これまで報告された高分子を用いた有機EL素子では保存中に素子にダークスポットと呼ばれる輝度の低い欠陥が発光面に生じ、表示品質の向上、保存時の表示品位の低下防止、ダークスポットの生成および成長の抑制が求められていた。ダークスポットを抑制するために、従来用いられていた方法は、固体や液体を電極に接触させるため、傷の発生による欠陥、不純物の拡散による劣化等が懸念された。また高価な材料を蒸着する等の方法で、低コストでの製造プロセ

スとはなり得なかった。

【0006】

【発明が解決しようとする課題】本発明の目的は、高分子を用いた高輝度、高発光効率、低駆動電圧の有機EL素子で、長期の保存においてもダークスポットがほとんど生成および成長しない有機エレクトロルミネッセンス素子を安価に提供することにある。

【0007】

【課題を解決するための手段】本発明者等は、このような事情をみて、高分子蛍光体を発光層として用いた有機EL素子の発光効率を向上させるために鋭意検討した結果、ポリアリーレンビニレン系高分子蛍光体からなる発光層を有する有機EL素子において、不活性気体で有機EL素子を保護することにより、高輝度、高発光効率の有機EL素子の保存特性が向上し、ダークスポットがほとんどが生成、成長しない有機エレクトロルミネッセンス素子が得られることを見出し、本発明に至った。

【0008】すなわち本発明は次に記す発明である。

〔1〕少なくとも一方が透明または半透明である一対の陽極および陰極からなる電極間に、少なくとも発光層を有する有機エレクトロルミネッセンス素子において、該発光層が固体状態で蛍光を有する高分子蛍光体を含み、該高分子蛍光体は、一般式(1)で示される繰返し単位を全繰返し単位の50モル%以上含み、ポリスチレン換算の数平均分子量が $10^3 \sim 10^7$ であり、該有機エレクトロルミネッセンス素子が、陽極表面からの間隔または陰極表面からの間隔が $1 \mu\text{m}$ 以上 2mm 以下である2枚の透明または半透明の板またはフィルムにより挟まれ、かつ外気と接触しないように隔絶されてなり、該素子と該板またはフィルムとの間の空間は不活性な気体で満たされてなることを特徴とする有機エレクトロルミネッセンス素子。

〔化2〕 $-\text{Ar}-\text{CR}=\text{CR}'-$ (1)

(ここで、Arは、共役結合に関与する炭素原子数が4個以上20個以下からなるアリーレン基または複素環化合物基であり、R、R'はそれぞれ独立に水素、炭素数1~20のアルキル基、炭素数6~20のアリール基、炭素数4~20の複素環化合物、シアノ基からなる群から選ばれる基を示す。)

【0009】〔2〕不活性な気体が、窒素、アルゴン、ヘリウムまたは二酸化炭素であることを特徴とする

〔1〕記載の有機エレクトロルミネッセンス素子。

〔3〕板またはフィルムが、陽極または陰極の基板であることを特徴とする〔1〕記載の有機エレクトロルミネッセンス素子。

〔4〕不活性な気体中で、透明または半透明な板またはフィルム上に作製した有機エレクトロルミネッセンス素子を囲むように、透明または半透明な板またはフィルム上に $1 \mu\text{m}$ 以上 2mm 以下のスペーサーを置き、この上から別の透明または半透明な板またはフィルムをのせ、スペーサーと2枚のそれぞれの透明または半透明な板またはフィルムとの接合部を光硬化型または熱硬化型接着剤で接合し、該接合部を光硬化または熱硬化させ、2枚の透明または半透明な板またはフィルムを接合することを特徴とする〔1〕記載の有機エレクトロルミネッセンス素子の製造方法。

【0010】本発明の有機EL素子は、少なくとも、アリーレンビニレン系高分子蛍光体からなる発光層と、前記有機EL素子を保護する不活性な気体層（以下、保護層ということがある。）とを有する。

【0011】本発明の有機EL素子の発光層に用いられる高分子蛍光体について説明する。該高分子蛍光体は、一般式(1)で示される繰返し単位を全繰返し単位の50モル%以上含む重合体である。繰返し単位の構造にもよるが、一般式(1)で示される繰返し単位が全繰返し単位の70%以上であることがさらに好ましい。該高分子蛍光体は、一般式(1)で示される繰返し単位以外の繰返し単位として、2価の芳香族化合物基もしくはその誘導体、2価の複素環化合物基もしくはその誘導体、またはそれらを組み合わせて得られる基などを含んでいてもよい。また、一般式(1)で示される繰返し単位や他の繰返し単位が、エーテル基、エステル基、アミド基、イミド基などを有する非共役の単位で連結されていてもよいし、繰返し単位にそれらの非共役部分が含まれていてもよい。

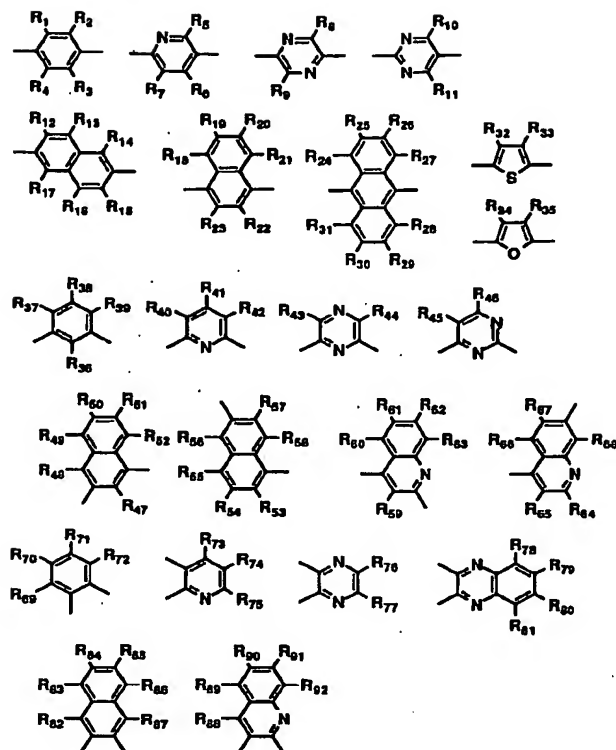
【0012】本発明における高分子蛍光体において一般式(1)のArとしては、共役結合に関与する炭素原子数が4個以上20個以下からなるアリーレン基または複素環化合物基であり、下記に示す2価の芳香族化合物基もしくはその誘導体基、2価の複素環化合物基もしくはその誘導体基、またはそれらを組み合わせて得られる基などが例示される。

【0013】

〔化3〕

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(R₁ ~ R₈₂は、それぞれ独立に、水素、炭素数1~20のアルキル基、アルコキシ基およびアルキルチオ基；炭素数6~18のアリール基およびアリールオキシ基；ならびに炭素数4~14の複素環化合物基からなる群から選ばれた基である。)

【0014】これらのなかでフェニレン基、置換フェニレン基、ビフェニレン基、置換ビフェニレン基、ナフタレンジイル基、置換ナフタレンジイル基、アントラセン-9, 10-ジイル基、置換アントラセン-9, 10-ジイル基、ピリジン-2, 5-ジイル基、置換ピリジン-2, 5-ジイル基、チエニレン基および置換チエニレン基が好ましい。さらに好ましくは、フェニレン基、ビフェニレン基、ナフタレンジイル基、ピリジン-2, 5-ジイル基、チエニレン基である。

【0015】一般式(1)のR、R'はそれぞれ独立に水素、炭素数1~20のアルキル基、炭素数6~20のアリール基、炭素数4~20の複素環化合物、シアノ基

からなる群から選ばれた基を示す。炭素数1~20のアルキル基としては、メチル基、エチル基、プロピル基、ブチル基、ペンチル基、ヘキシル基、ヘプチル基、オクチル基、デシル基、ラウリル基などが挙げられ、メチル基、エチル基、ペンチル基、ヘキシル基、ヘプチル基、オクチル基が好ましい。アリール基としては、フェニル基、4-C₁~C₁₂アルコキシフェニル基(C₁~C₁₂は、炭素数が1~12のいずれかの数であることを示す。)、4-C₁~C₁₂アルキルフェニル基、1-ナフチル基、2-ナフチル基などが例示される。

【0016】溶媒可溶性の観点からは一般式(1)のArが、炭素数4~20のアルキル基、アルコキシ基およびアルキルチオ基、炭素数6~18のアリール基およびアリールオキシ基ならびに炭素数4~14の複素環化合物基から選ばれた基を1つ以上有していることが好ましい。

【0017】具体的には、炭素数4~20のアルキル基

としては、ブチル基、ペンチル基、ヘキシル基、ヘプチル基、オクチル基、デシル基、ラウリル基などが挙げられ、ペンチル基、ヘキシル基、ヘプチル基、オクチル基が好ましい。また、炭素数4~20のアルコキシ基としては、ブトキシ基、ペンチルオキシ基、ヘキシルオキシ基、ヘプチルオキシ基、オクチルオキシ基、デシルオキシ基、ラウリルオキシ基などが挙げられ、ペンチルオキシ基、ヘキシルオキシ基、ヘプチルオキシ基、オクチルオキシ基が好ましい。アルキルチオ基としては、ブチルチオ基、ペンチルチオ基、ヘキシルチオ基、ヘプチルチオ基、オクチルチオ基、デシルオキシ基、ラウリルチオ基などが挙げられ、ペンチルチオ基、ヘキシルチオ基、ヘプチルチオ基、オクチルチオ基が好ましい。アリール基としては、フェニル基、4-C₁~C₁₂アルコキシフェニル基、4-C₁~C₁₂アルキルフェニル基、1-ナフチル基、2-ナフチル基などが例示される。アリールオキシ基としては、フェノキシ基が例示される。複素環化合物基としては2-チエニル基、2-ピロリル基、2-フリル基、2-, 3-または4-ピリジル基などが例示される。これら置換基の数は、該高分子蛍光体の分子量と繰り返し単位の構成によっても異なるが、溶解性の高い高分子蛍光体を得る観点から、これらの置換基が分子量600当たり1つ以上であることが好ましい。

【0018】なお、本発明の有機EL素子に用いる高分子蛍光体は、ランダム、ブロックまたはグラフト共重合体であってもよいし、それらの中間的な構造を有する高分子、例えばブロック性を帯びたランダム共重合体であってもよい。蛍光の量子収率の高い高分子蛍光体を得る観点からは完全なランダム共重合体よりブロック性を帯びたランダム共重合体やブロックまたはグラフト共重合体が好ましい。また、本発明の有機EL素子は、薄膜からの発光を利用するので該高分子蛍光体は、固体状態で発光を有するものが用いられる。

【0019】該高分子蛍光体に対する良溶媒としては、クロロホルム、塩化メチレン、ジクロロエタン、テトラヒドロフラン、トルエン、キシレンなどが例示される。高分子蛍光体の構造や分子量にもよるが、通常はこれらの溶媒に0.1wt%以上溶解させることができる。

【0020】本発明における高分子蛍光体は、分子量がポリスチレン換算で10³~10⁷であり、それらの重合度は繰り返し構造やその割合によっても変わる。成膜性の点から一般には繰り返し構造の合計数で好ましくは4~10000、さらに好ましくは5~3000、特に好ましくは10~2000である。

【0021】有機EL素子作成の際に、これらの有機溶媒可溶性の高分子蛍光体を用いることにより、溶液から成膜する場合、この溶液を塗布後乾燥により溶媒を除去するだけでよく、また後述するさらに電荷輸送材料や発光材料を混合した場合においても同様な手法が適用でき、製造上非常に有利である。

【0022】本発明の有機EL素子に用いる高分子蛍光体の合成法としては特に限定されないが、例えば、アリーレン基にアルデヒド基が2つ結合したジアルデヒド化合物と、アリーレン基にハロゲン化メチル基が2つ結合した化合物とトリフェニルホスフィンとから得られるジホスホニウム塩からのWittig反応が例示される。また、他の合成法としては、アリーレン基にハロゲン化メチル基が2つ結合した化合物からの脱ハロゲン化水素法が例示される。さらに、アリーレン基にハロゲン化メチル基が2つ結合した化合物のスルホニウム塩をアルカリで重合して得られる中間体から熱処理により該高分子蛍光体を得るスルホニウム塩分解法が例示される。いずれの合成法においても、モノマーとして、アリーレン基以外の骨格を有する化合物を加え、その存在割合を変えることにより、生成する高分子蛍光体に含まれる繰り返し単位の構造を変えることができるので、一般式(1)で示される繰り返し単位が50モル%以上となるように加減して仕込み、共重合してもよい。これらのうち、Wittig反応による方法が、反応の制御や収率の点で好ましい。

【0023】さらに具体的に、本発明の有機EL素子に用いられる高分子蛍光体の1つの例であるアリーレンビニレン系共重合体の合成法を説明する。Wittig反応により高分子蛍光体を得る場合は、例えばまず、ビス(ハロゲン化メチル)化合物、より具体的には、例えば、2,5-ジオクチルオキシ-p-キシリレンジブロミドをN,N-ジメチルホルムアミド溶液中、トリフェニルホスフィンと反応させてホスホニウム塩を合成し、これとジアルデヒド化合物、より具体的には、例えば、テレフタルアルデヒドとを、例えばエチルアルコール中、リチウムエトキシドを用いて縮合させるWittig反応により、フェニレンビニレン基と2,5-ジオクチルオキシ-p-フェニレンビニレン基を含む高分子蛍光体を得られる。この時、共重合体を得るために2種類以上のジホスホニウム塩および/または2種類以上のジアルデヒド化合物を反応させてもよい。

【0024】これらの高分子蛍光体を有機EL素子の発光材料として用いる場合、その純度が発光特性に影響を与えるため、合成後、再沈精製、クロマトグラフによる分別等の純化処理をすることが望ましい。

【0025】次に本発明の有機EL素子に用いられる保護層について説明する。本発明の有機EL素子は、陽極表面からの間隔または陰極表面からの間隔が1μm以上2mm以下、好ましくは100μm以上1mm以下である2枚の透明または半透明の板またはフィルムにより挟まれ、かつ外気と接触しないように隔絶されている。具体的には、該素子として2枚の透明または半透明の板またはフィルムとこの2枚の板またはフィルムを接合する接合部からなる被覆体により覆われ、外気と接触しないように隔絶されている例が挙げられる。該素子を2枚の

板またはフィルムの双方に直接接合させると素子にクラックが発生することがあるので好ましくない。該板またはフィルムに用いる材料としては、ガラス、ポリエチレンテレフタレート（PET）、防湿性フィルムなどが挙げられ、ガラス、防湿性フィルムが空気中の水分、酸素を透過しにくいので好ましい。

【0026】該素子と該板またはフィルムとの間の空間、例えば該素子と該被覆体との間の空間は不活性な気体で満たされている。不活性な気体としては、窒素、アルゴン、ヘリウムまたは二酸化炭素が好ましく、アルゴン、窒素がさらに好ましい。なお、不活性な気体中の水分量は、素子の劣化を防ぐため 1000ppm 以下が好ましく、100ppm 以下がさらに好ましい。

【0027】本発明の有機EL素子の構造については、少なくとも一方が透明または半透明である一対の電極間に設ける発光層中に前述の高分子蛍光体が用いられており、かつ保護層として、該有機EL素子を外気と接触しないよう隔絶するため、不活性な気体で満たされた 1μm 以上 2mm 以下の空間で隔てられた 2 枚の透明または半透明の板またはフィルムで覆われていれば、特に制限はなく、公知の構造が採用される。例えば、該高分子蛍光体からなる発光層、もしくは該高分子蛍光体と電荷輸送材料（電子輸送材料と正孔輸送材料の総称を意味する）との混合物からなる発光層の両面に一対の電極を有する構造のもの、発光層と陽極との間に正孔輸送材料を含有する正孔輸送層を積層したもの、発光層と陰極との間に電子輸送材料を含有する電子輸送層を積層したもの、さらに発光層と陽極との間に正孔輸送材料を含有する正孔輸送層を積層し、かつ発光層と陰極との間に電子輸送材料を含有する電子輸送層を積層したもの等が例示される。また、発光層や電荷輸送層について、1 層の場合も複数の層を組み合わせる場合も本発明に含まれる。さらに、発光層に例えば該高分子蛍光体以外の下記に述べる発光材料を混合使用してもよい。また、該高分子蛍光体および／または電荷輸送材料を高分子化合物に分散させた層とすることもできる。

【0028】本発明の高分子蛍光体とともに使用される電荷輸送材料、すなわち、電子輸送材料または正孔輸送材料としては公知のものが使用でき、特に限定されないが、正孔輸送材料としてはピラゾリン誘導体、アリアルアミン誘導体、スチルベン誘導体、トリフェニルジアミン誘導体等が、電子輸送材料としてはオキサジアゾール誘導体、アントラキノジメタンおよびその誘導体、ベンゾキノロンおよびその誘導体、ナフトキノロンおよびその誘導体、アントラキノロンおよびその誘導体、テトラシアノアンスラキノジメタンおよびその誘導体、フルオレノン誘導体、ジフェニルジシアノエチレンおよびその誘導体、ジフェノキノロン誘導体、8-ヒドロキシキノリンおよびその誘導体の金属錯体等が例示される。

【0029】具体的には、特開昭 63-70257号、

同 63-175860 号公報、特開平 2-135359 号、同 2-135361 号、同 2-209988 号、同 3-37992 号、同 3-152184 号公報に記載されているもの等が例示される。正孔輸送材料としてはトリフェニルジアミン誘導体、電子輸送材料としてはオキサジアゾール誘導体、ベンゾキノロンおよびその誘導体、アントラキノロンおよびその誘導体、8-ヒドロキシキノリンおよびその誘導体の金属錯体が好ましく、特に、正孔輸送材料としては 4, 4'-ビス（N（3-メチルフェニル）-N-フェニルアミノ）ビフェニル、電子輸送材料としては 2-（4-ビフェニル）-5-（4-tert-ブチルフェニル）-1, 3, 4-オキサジアゾール、ベンゾキノロン、アントラキノロン、トリス（8-キノリノール）アルミニウムが好ましい。これらのうち、電子輸送性の化合物と正孔輸送性の化合物のいずれか一方、または両方を同時に使用すればよい。これらは単独で用いてもよいし、2 種類以上を混合して用いてもよい。

【0030】発光層と電極との間にさらに電荷輸送層を設ける場合、これらの電荷輸送材料を使用して電荷輸送層を形成すればよい。また、電荷輸送材料を発光層に混合して使用する場合、電荷輸送材料の使用量は使用する化合物の種類等によっても異なるので、十分な成膜性と発光特性を阻害しない範囲でそれらを考慮して適宜決めればよい。通常、発光材料に対して 1~40 重量%であり、さらに好ましくは 2~30 重量%である。

【0031】本発明における高分子蛍光体と共に使用できる公知の発光材料としては特に限定されないが、例えば、ナフタレン誘導体、アントラセンおよびその誘導体、ペリレンおよびその誘導体、ポリメチン系、キサンテン系、クマリン系、シアニン系などの色素類、8-ヒドロキシキノリンおよびその誘導体の金属錯体、芳香族アミン、テトラフェニルシクロペンタジエンおよびその誘導体、テトラフェニルブタジエンおよびその誘導体などを用いることができる。具体的には、例えば特開昭 57-51781 号公報、同 59-194393 号公報に記載されているもの等が使用可能である。

【0032】次に、本発明の発光材料を用いた有機EL素子の代表的な作製方法について、図 1 に基づいて述べる。なお、陽極および陰極のパターンについては、公知のパターンを用いることができるため、図 1 ではそのパターンの詳細は省略している。また、図 1 においては、2 枚の透明または半透明の板またはフィルムの 1 枚が陽極の基板を兼ねている場合に相当する。陽極 4 としては、ガラス、透明プラスチック等の透明または半透明の板またはフィルム 1 の上に、透明または半透明の電極を形成したものが用いられる。陽極 4 の材料としては、導電性の金属酸化物膜、半透明の金属薄膜等が用いられる。具体的にはインジウム・スズ・オキサイド（ITO）、酸化スズ等からなる導電性ガラスを用いて作成された膜（NE SA など）、金、白金、銀、銅等が用いら

れる。作製方法としては真空蒸着法、スパッタリング法、メッキ法などが用いられる。陰極8としても、同様のものが用いられる。

【0033】この陽極4上に、発光材料として上記高分子蛍光体、または該高分子蛍光体と電荷輸送材料を含む発光層6を形成する。形成方法としては、これら材料の熔融液、溶液または混合液を使用してスピンコーティング法、キャスト法、ディッピング法、バーコート法、ロールコート法等の塗布法が例示されるが、溶液または混合液を用いて成膜することが特に好ましい。

【0034】発光層6の膜厚としては好ましくは1nm～1μm、さらに好ましくは2nm～500nmである。電流密度を上げて発光効率を上げるためには5～200nmの範囲が好ましい。なお、発光層6を塗布法により薄膜化した場合には、溶媒を除去するため、発光層形成後に、減圧下または不活性雰囲気下、30～300℃、好ましくは60～200℃の温度で加熱乾燥することが望ましい。

【0035】該発光層6の下に正孔輸送層5を積層する場合(図1に示す場合)には、上記の成膜方法で発光層6を設ける前に、正孔輸送層5を形成することが好ましい。正孔輸送層5の成膜方法としては、特に限定されないが、粉末状態からの真空蒸着法、または溶液に溶かした後のスピンコーティング法、キャスト法、ディッピング法、バーコート法、ロールコート法等の塗布法、または高分子化合物と電荷輸送材料とを溶液状態または熔融状態で混合し分散させた後のスピンコーティング法、キャスト法、ディッピング法、バーコート法、ロールコート法等の塗布法を用いることができる。

【0036】混合する高分子化合物としては、特に限定されないが、電荷輸送を極度に阻害しないものが好ましく、また可視光に対する吸収が強いものが好適に用いられる。例えば、ポリ(N-ビニルカルバゾール)、ポリアニリンおよびその誘導体、ポリチオフェンおよびその誘導体、ポリ(p-フェニレンビニレン)およびその誘導体、ポリ(2,5-チエニレンビニレン)およびその誘導体、ポリカーボネート、ポリアクリレート、ポリメチルアクリレート、ポリメチルメタクリレート、ポリスチレン、ポリ塩化ビニル、ポリシロキサンなどが例示される。成膜が容易に行なえるという点では、高分子化合物を用いる場合は塗布法を用いることが好ましい。

【0037】正孔輸送層5の膜厚は、少なくともピンホールが発生しないような厚みが必要であるが、あまり厚いと、素子の抵抗が増加し、高い駆動電圧が必要となり好ましくない。したがって、電荷輸送層の膜厚は好ましくは1nm～1μm、さらに好ましくは2nm～500nm、特に好ましくは5～200nmである。

【0038】また、該発光層の上にさらに電子輸送層7を積層する場合(図1に示す場合)には、上記の成膜方法で発光層6を設けた後にその上に電子輸送層7を形成

することが好ましい。

【0039】電子輸送層7の成膜方法としては、特に限定されないが、粉末状態からの真空蒸着法、または溶液に溶かした後のスピンコーティング法、キャスト法、ディッピング法、バーコート法、ロールコート法等の塗布法、または高分子化合物と電荷輸送材料とを溶液状態もしくは熔融状態で混合し分散させた後のスピンコーティング法、キャスト法、ディッピング法、バーコート法、ロールコート法等の塗布法を用いることができる。

【0040】混合する高分子化合物としては、特に限定されないが、電荷輸送を極度に阻害しないものが好ましく、また可視光に対する吸収が強いものが好適に用いられる。例えば、ポリ(N-ビニルカルバゾール)、ポリアニリンおよびその誘導体、ポリチオフェンおよびその誘導体、ポリ(p-フェニレンビニレン)およびその誘導体、ポリ(2,5-チエニレンビニレン)およびその誘導体、ポリカーボネート、ポリアクリレート、ポリメチルアクリレート、ポリメチルメタクリレート、ポリスチレン、ポリ塩化ビニル、ポリシロキサンなどが例示される。成膜が容易に行なえるという点では、高分子化合物を用いる場合は塗布法を用いることが好ましい。電子輸送層7の膜厚は、少なくともピンホールが発生しないような厚みが必要であるが、あまり厚いと、素子の抵抗が増加し、高い駆動電圧が必要となり好ましくない。したがって、電荷輸送層の膜厚は好ましくは1nm～1μm、さらに好ましくは2nm～500nm、特に好ましくは5～200nmである。

【0041】次いで、発光層6または電子輸送層7の上に陰極8を設ける。該陰極8は電子注入陰極となる。その材料としては、特に限定されないが、イオン化エネルギーの小さい材料が好ましい。例えば、アルミニウム、インジウム、マグネシウム、カルシウム、リチウム、マグネシウム-銀合金、マグネシウム-インジウム合金、マグネシウム-インジウム合金、リチウム-アルミニウム合金、リチウム-銀合金、リチウム-インジウム合金またはグラファイト薄膜等が用いられる。陰極の作製方法としては真空蒸着法、スパッタリング法等が用いられる。

【0042】次に、本発明における有機EL素子の保護層の製造方法の1例について図1に基づいて説明する。以下の操作を不活性な気体中で行なうことにより、該有機EL素子と透明または半透明な板またはフィルムとの間の空間、すなわち該有機EL素子と被覆体との間の空間が不活性な気体9で満たされる。まず、前記のように透明または半透明な板またはフィルム1(基板を兼ねる。)上に作製した有機エレクトロルミネッセンス素子を囲むように、透明または半透明な板またはフィルム1(基板を兼ねる。)上に1μm以上2mm以下のスペーサー3を置き、この上から別の透明または半透明な板ま

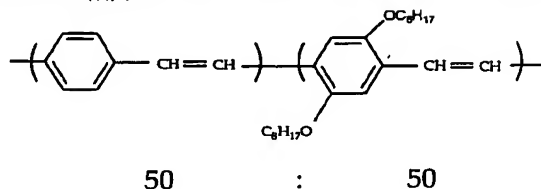
たはフィルム10をのせる。次に、スペーサー3と2枚のそれぞれの透明または半透明な板またはフィルムとの接合部を光硬化型または熱硬化型接着剤2で接合し、該接合部を光硬化または熱硬化させ、2枚の透明または半透明な板またはフィルムを接合する。これにより、有機EL素子は外気と遮断される。

【0043】

【作用】本発明の有機EL素子が優れているのは、融点や分解温度が比較的高い高分子材料を用いているので熱的に安定であり、塗布法により容易に発光層を形成することによる。このため非常に容易に高輝度、高発光効率の有機EL素子を作製することができる。さらに、本発明で用いる保護層の作用により、特に陰極の耐久性が高いので長寿命化ができ、ダークスポットの生成を抑える効果があると考えられる。

【0044】

【実施例】以下、本発明の実施例を示すが、本発明はこれらに限定されるものではない。ここで、数平均分子量については、クロロホルムを溶媒として、ゲルパーミエ



ここで、二つの繰返し単位は交互に結合している。該高分子蛍光体1のポリスチレン換算の数平均分子量は、 1.0×10^4 であった。該高分子蛍光体1の構造については赤外吸収スペクトル、NMRで確認した。

【0045】＜素子の作成および評価＞スパッタリングによって、40nmの厚みでITO膜を付けたガラス基板に、ポリビニルカルバゾールの1.0wt%クロロホルム溶液を用いて、ディッピングにより50nmの厚みで成膜した。さらに、高分子蛍光体1の1.0wt%トルエン溶液を用いて、スピンコートにより50nmの厚みで成膜した。さらに、これを減圧下150℃で1時間乾燥した後、電子輸送層として、トリス(8-キノリノール)アルミニウム(Alq₃)を0.1~0.2nm/sの速度で35nm蒸着した。その上に陰極の第1の金属層としてリチウム-アルミニウム合金(リチウム濃度:1wt%)を40nm蒸着して有機EL素子を作製した。蒸着のときの真空度はすべて 8×10^{-6} Torr以下であった。電極作製後、窒素雰囲気中で、透明基板上に作製した有機EL素子の周囲に1mmのガラスのスペーサーを置き、この上からガラス板をのせ、スペーサー一部を光硬化型接着剤を用い、基板と該ガラス板とを接合することにより有機EL素子保護層を作製した。この素子に電圧12.5Vを印加したところ、電流密度3

ーションクロマトグラフィー(GPC)によりポリスチレン換算の数平均分子量を求めた。

実施例1

＜高分子蛍光体1の合成＞2, 5-ジオクチルオキシ-p-キシリレンジブロミドをN, N-ジメチルホルムアミド溶媒中、トリフェニルホスフィンと反応させてホスホニウム塩を合成した。得られたホスホニウム塩47.75重量部、およびテレフタルアルデヒド6.7重量部を、エチルアルコールに溶解させた。5.8重量部のリチウムエトキシドを含むエチルアルコール溶液をホスホニウム塩とジアルデヒドのエチルアルコール溶液に滴下し、室温で3時間重合させた。一夜室温で放置した後、沈殿を濾別し、エチルアルコールで洗浄後、クロロホルムに溶解、これにエタノールを加え再沈生成した。これを減圧乾燥して、重合体8.0重量部を得た。これを高分子蛍光体1という。モノマーの仕込み比から計算される高分子蛍光体1の繰返し単位とそのモル比を下記に示す。

【化4】

2.1mA/cm²の電流が流れ、輝度1892cd/m²の黄緑色のEL発光が観察された。この時の発光効率は、5.9cd/Aであった。輝度はほぼ電流密度に比例していた。また、ELピーク波長は540nmで、高分子蛍光体1の薄膜の蛍光ピーク波長とほぼ一致しており高分子蛍光体1よりのEL発光が確認された。この素子を空気中で5日間保存後、10Vで低電圧駆動したところ、ダークスポットの発生は少なく、非発光部分の面積は10%以下であった。

【0046】比較例1

有機EL素子の保護層を用いない以外は、実施例1と同じ方法で素子を作成した。この素子に電圧12.5Vを印加したところ、電流密度32.1mA/cm²の電流が流れ、輝度1892cd/m²の黄緑色のEL発光が観察された。この時の発光効率は、5.9cd/Aであった。輝度はほぼ電流密度に比例していた。また、ELピーク波長は540nmで、高分子蛍光体1の薄膜の蛍光ピーク波長とほぼ一致しており高分子蛍光体1よりのEL発光が確認された。この素子を空気中で5日間保存後、10Vで低電圧駆動したところ、ダークスポットの発生が多く、非発光部分の面積は約50%程度であった。

【0047】このように、実施例1の有機EL素子が、

不活性な気体で満たされた1mmの空間で隔てられた2枚のガラス板で覆われている有機EL素子は、不活性な気体で満たされた1mmの空間で隔てられた2枚のガラス板で覆われてない比較例1の有機EL素子よりも、ダークスポットの発生が少なく、優れた発光表示品位の保存特性を示した。

【0048】

【発明の効果】本発明の高分子蛍光体と陰極とを不活性な気体で満たされた1 μ m以上2mm以下の空間と、それらを覆うカバーで、外気と接触しないよう隔絶されている有機エレクトロルミネッセンス素子は、作成が容易で、また優れた発光表示品位の保存特性を示すので、バックライトとしての面状光源、フラットパネルディスプレイ等の装置として好ましく使用できる。

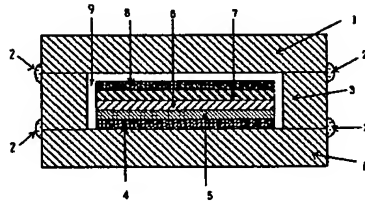
【図面の簡単な説明】

【図1】本発明の有機エレクトロルミネッセンス素子の1例の層構成を示す断面図。

【符号の説明】

- 1 透明または半透明な板またはフィルム。
- 2 光硬化型または熱硬化型接着剤。
- 3 スペーサー。
- 4 陽極（透明電極）。
- 5 正孔輸送層。
- 6 発光層。
- 7 電子輸送層。
- 8 陰極。
- 9 不活性気体。

【図1】



フロントページの続き

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 CLAIMS

[Claim(s)]

[Claim 1] In the organic electroluminescent element which has a luminous layer at least in inter-electrode [which at least one side becomes from the anode plate and cathode of a transparent or translucent couple] The macromolecule fluorescent substance with which this luminous layer has fluorescence by the solid state is included. this macromolecule fluorescent substance The repeat unit shown by the general formula (1) A 50 mol % not-less implication of all repeat units, the number average molecular weight of polystyrene conversion -- 103-107 it is -- this organic electroluminescent element Be caught with transparent or translucent the board or film the interval from an anode plate front face or whose interval from a cathode surface is two sheets it is [sheets] 1 micrometers or more 2mm or less. And it is the organic electroluminescent element which is isolated, becomes so that the open air may not be contacted, and the space between this element, this board, or a film is filled with an inactive gas, and is characterized by the bird clapper.

[Formula 1] $-Ar-CR=CR'-$ (1)

(Here, Ar is the arylene machine or heterocyclic-compound machine with which the carbon atomic number which participates in conjugate combination consists of four or more pieces [20 or less], and R and R' shows the basis chosen from the group which consists of hydrogen, the alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, a heterocyclic compound of carbon numbers 4-20, and a cyano group independently, respectively.)

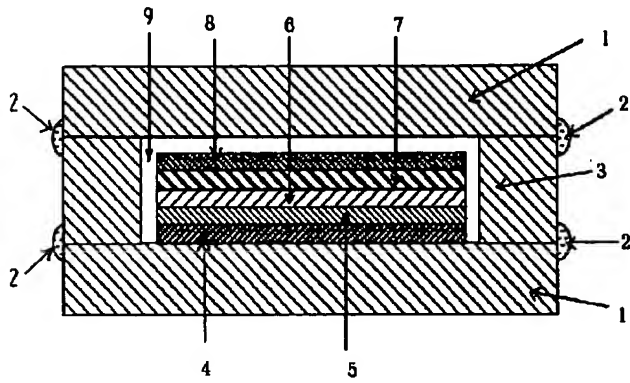
[Claim 2] Organic electroluminescent element according to claim 1 to which an inactive gas is characterized by being nitrogen, an argon, helium, or a carbon dioxide.

[Claim 3] Organic electroluminescent element according to claim 1 to which a board or a film is characterized by being the substrate of an anode plate or cathode.

[Claim 4] So that the organic electroluminescent element produced on the board transparent or translucent in an inactive gas or the film may be surrounded 1-micrometer or more spacer 2mm or less is placed on a transparent or translucent board or a film. Carry transparent or translucent an another board or an another film from besides, and a joint with a spacer, each two transparent or translucent boards, or a film is joined with an optical hardening type or heat-hardened type adhesives. The manufacture method of the organic electroluminescent element according to claim 1 characterized by light-hardening, or making this joint heat-harden, and joining two transparent or translucent boards or a film.

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Drawing selection ☒ [Representative drawing]



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[0004] About the organic EL element using the low-molecular organic fluorochrome, the organic EL element which used for the metallic material of cathode liquid material, such as independent material or the solid material by which vapor codeposition was carried out, such as an indium and an aluminum quinolinol complex, a silicone oil, and fluorination carbon, as a protective layer of an electrode as a protective layer is indicated by JP,5-101892,A, 159881, and the No. 129080 or 41281 official report.

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preservation, the low defect of the brightness called dark spot to an element arose in the luminescence side, and improvement in display quality, fall prevention of the display grace at the time of preservation, generation of a dark spot, and suppression of growth were called for. In order that the method conventionally used in order to suppress a dark spot might contact a solid-state and a liquid to an electrode, we were anxious about degradation by diffusion of the defect by generating of a blemish, and an impurity etc. Moreover, by carrying out the vacuum evaporation of the expensive material etc., it could not become a manufacture process in a low cost.

[0006]

[Problem(s) to be Solved by the Invention] The purposes of this invention are the high brightness and high luminous efficiency which used the macromolecule, and the organic EL element of low driver voltage, and are to offer cheaply the organic electroluminescent element also set to long-term preservation, and a dark spot hardly generates and grows up to be.

[0007]

[Means for Solving the Problem] The result wholeheartedly examined in order that this invention person etc. might see such a situation and might raise the luminous efficiency of the organic EL element using the macromolecule fluorescent substance as a luminous layer, In the organic EL element which has the luminous layer which consists of a poly arylene vinylene system macromolecule fluorescent substance By protecting an organic EL element by the inert gas, high brightness and the preservation property of the organic EL element of high luminous efficiency improved, and it found out that the organic electroluminescent element most does not generate and a dark spot does not grow up to be was obtained, and resulted in this invention.

[0008] That is, this invention is invention described below.

[1] In the organic electroluminescent element which has a luminous layer at least in inter-electrode [which at least one side becomes from the anode plate and cathode of a transparent or translucent couple] The macromolecule fluorescent substance with which this luminous layer has fluorescence by the solid state is included. this macromolecule fluorescent substance The repeat unit shown by the general formula (1) A 50 mol % not-less implication of all repeat units, the number average molecular weight of polystyrene conversion -- 103-107 it is -- this organic electroluminescent element Be caught with transparent or translucent the board or film the interval from an anode plate front face or whose interval from a cathode surface is two sheets it is [sheets] 1 micrometers or more 2mm or less. And it is the organic electroluminescent element which is isolated, becomes so that the open air may not be contacted, and the space between this element, this board, or a film is filled with an inactive gas, and is characterized by the bird clapper.

[Formula 2] -Ar-CR=CR'- (1)

(Here, Ar is the arylene machine or heterocyclic-compound machine with which the carbon atomic number which participates in conjugate combination consists of four or more pieces [20 or less], and R and R' shows the basis chosen from the group which consists of hydrogen, the alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, a heterocyclic compound of carbon numbers 4-20, and a cyano group independently, respectively.)

[0009] [2] Organic electroluminescent element given in [1] to which an inactive gas is characterized by being nitrogen, an argon, helium, or a carbon dioxide.

[3] Organic electroluminescent element given in [1] to which a board or a film is characterized by being the substrate of an anode plate or cathode.

[4] So that the organic electroluminescent element produced on the board transparent or translucent in an inactive gas or the film may be surrounded 1-micrometer or more spacer 2mm or less is placed on a transparent or translucent board or a film. Carry transparent or translucent an another board or an another film from besides, and a joint with a spacer, each two transparent or translucent boards, or a film is joined with an optical hardening type or heat-hardened type adhesives. The manufacture method of the organic electroluminescent element given in [1] characterized by light-hardening, or making this joint heat-harden, and joining two transparent or translucent boards or a film.

[0010] The organic EL element of this invention has at least the luminous layer which consists of an

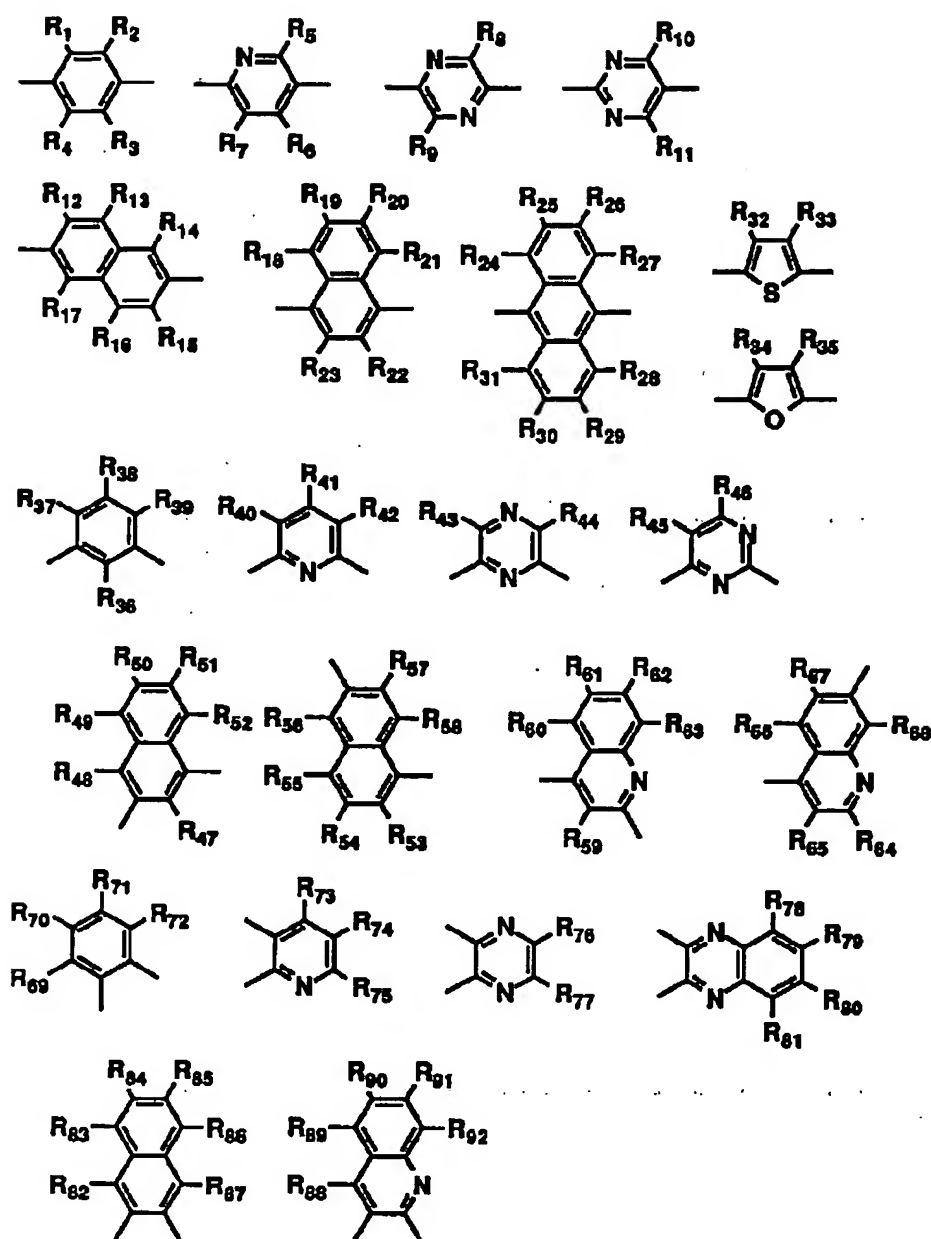
arylene vinylene system macromolecule fluorescent substance, and the inactive gas layer (it may be hereafter called a protective layer) which protects the aforementioned organic EL element.

[0011] The macromolecule fluorescent substance used for the luminous layer of the organic EL element of this invention is explained. the repeat unit this macromolecule fluorescent substance is indicated to be by the general formula (1) -- more than 50 mol % of all repeat units -- it is the included polymer. Although based also on the structure of a repeat unit, it is still more desirable that the repeat units shown by the general formula (1) are 70% or more of all repeat units. This macromolecule fluorescent substance may contain a divalent aromatic compound machine or its derivative, a divalent heterocyclic-compound machine, its derivative, or the basis obtained combining them as repeat units other than the repeat unit shown by the general formula (1). Moreover, the repeat unit shown by the general formula (1) and other repeat units may be connected in the disconjugation unit which has an ether machine, an ester machine, an amide group, an imido basis, etc., and those disconjugation portions may be contained per repeat.

[0012] The carbon atomic number which participates in conjugate combination as Ar of a general formula (1) in the macromolecule fluorescent substance in this invention is the arylene machine or heterocyclic-compound machine which consists of four or more pieces [20 or less], and the divalent aromatic compound machine shown below, the derivative machine and a divalent heterocyclic-compound machine, its derivative machine, or the basis obtained combining them is illustrated.

[0013]

[Formula 3]



(R1 -R92 are the basis independently chosen from the group which becomes hydrogen, the alkyl group of carbon numbers 1-20, an alkoxy group, the aryl group of the alkyl thio basis; carbon numbers 6-18, and an aryloxy group; row from the heterocyclic-compound machine of carbon numbers 4-14, respectively.)

[0014] A phenylene group, a substitution phenylene group, a biphenylene machine, a substitution biphenylene machine, a naphthalene diyl machine, a substitution naphthalene diyl machine, an anthracene -9, 10-diyl machine, the substitution anthracene -9, 10-diyl machine, a pyridine -2, 5-diyl machine, the substitution pyridine -2, 5-diyl machine, a thienylene machine, and a substitution thienylene machine are desirable in these. They are a phenylene group, a biphenylene machine, a naphthalene diyl machine, a pyridine -2, 5-diyl machine, and a thienylene machine still more preferably.

[0015] R of a general formula (1) and R' show the basis chosen from the group which consists of hydrogen, the alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, a heterocyclic compound of carbon numbers 4-20, and a cyano group independently, respectively. As an alkyl group of carbon numbers 1-20, a methyl group, an ethyl group, a propyl group, a butyl, a pentyl

machine, a hexyl machine, a heptyl machine, an octyl machine, a decyl group, a lauryl machine, etc. are mentioned, and a methyl group, an ethyl group, a pentyl machine, a hexyl machine, a heptyl machine, and an octyl machine are desirable. As an aryl group, a phenyl group, a 4-C1 - C12 alkoxy phenyl group (C1 -C12 show that a carbon number is the number of either 1-12.), 4-C1 - C12 alkylphenyl machine, 1-naphthyl group, 2-naphthyl group, etc. are illustrated.

[0016] It is desirable that Ar of a general formula (1) has one or more bases chosen as the alkyl group of carbon numbers 4-20, the alkoxy group and the alkyl thio machine, the aryl group of carbon numbers 6-18, and the aryloxy group row from the heterocyclic-compound machine of carbon numbers 4-14 from a viewpoint of solvent fusibility.

[0017] Specifically, as an alkyl group of carbon numbers 4-20, a butyl, a pentyl machine, a hexyl machine, a heptyl machine, an octyl machine, a decyl group, a lauryl machine, etc. are mentioned, and a pentyl machine, a hexyl machine, a heptyl machine, and an octyl machine are desirable. Moreover, as an alkoxy group of carbon numbers 4-20, a butoxy machine, a pentyloxy machine, a hexyloxy machine, a heptyloxy machine, an octyloxy machine, a decyloxy machine, a lauryl oxy-basis, etc. are mentioned, and a pentyloxy machine, a hexyloxy machine, a heptyloxy machine, and an octyloxy machine are desirable. As an alkyl thio machine, a butyl thio machine, a pentyl thio machine, a hexyl thio machine, a heptyl thio machine, an octyl thio machine, a decyloxy machine, a laurylthio machine, etc. are mentioned, and a pentyl thio machine, a hexyl thio machine, a heptyl thio machine, and an octyl thio machine are desirable. As an aryl group, a phenyl group, a 4-C1 - C12 alkoxy phenyl group, 4-C1 - C12 alkylphenyl machine, 1-naphthyl group, 2-naphthyl group, etc. are illustrated. A phenoxy machine is illustrated as an aryloxy group. As a heterocyclic-compound machine, 2-thienyl group, 2-pyrrolyl machine, 2-furyl machine, 2-, 3-, or 4-pyridyl machine is illustrated. Although the number of these substituents differs from the molecular weight of this macromolecule fluorescent substance also by composition of a unit repeatedly, it is desirable that the viewpoint which obtains a soluble high macromolecule fluorescent substance to these substituents are one or more per molecular weight 600.

[0018] In addition, the macromolecule fluorescent substance used for the organic EL element of this invention may be randomness, a block, or a graft copolymer, and may be the macromolecule which has those middle-structures, for example, the random copolymer which wore block nature. From a viewpoint which obtains the high macromolecule fluorescent substance of the quantum yield of fluorescence, a random copolymer, and the block or graft copolymer which wore block nature is more desirable than a perfect random copolymer. Moreover, since the organic EL element of this invention uses luminescence from a thin film, that in which this macromolecule fluorescent substance has fluorescence by the solid state is used.

[0019] As a good solvent to this macromolecule fluorescent substance, chloroform, a methylene chloride, a dichloroethane, a tetrahydrofuran, toluene, a xylene, etc. are illustrated. although based also on the structure and molecular weight of a macromolecule fluorescent substance -- usually -- these solvents -- more than 0.1wt% -- it can be made to dissolve

[0020] The molecular weight of the macromolecule fluorescent substance in this invention is 103-107 in polystyrene conversion, and those polymerization degree changes also with repeat structure or its rate. general [from the point of membrane formation nature] -- the total number of repeat structure -- desirable -- 4-10000 -- further -- desirable -- 5-3000 -- it is 10-2000 especially preferably

[0021] When forming membranes from a solution by using the macromolecule fluorescent substance of such organic-solvent fusibility, in the case of organic EL-element creation, when [which mentions this solution later that what is necessary is just for the dryness after an application to remove a solvent] charge transportation material and luminescent material are mixed further, the same technique can be applied, and it is very advantageous to it on manufacture.

[0022] Although not limited especially as a synthesis method of the macromolecule fluorescent substance used for the organic EL element of this invention, the Wittig reaction from the diphosphonium salt obtained from the dialdehyde compound which two aldehyde groups combined with the arylene machine, the compound which two halogenation methyl groups combined with the arylene machine, and triphenyl phosphine, for example is illustrated. Moreover, as other synthesis methods, the

dehydrohalogenation method from the compound which two halogenation methyl groups combined with the arylene machine is illustrated. Furthermore, the sulfonium salinity solution method which obtains this macromolecule fluorescent substance from the intermediate field obtained by carrying out the polymerization of the sulfonium salt of the compound which two halogenation methyl groups combined with the arylene machine with alkali with heat treatment is illustrated. Since the structure of the repeat unit included in the macromolecule fluorescent substance generated by adding as a monomer the compound which has skeletons other than an arylene machine also in which synthesis method, and changing the abundance is changeable, you may adjust, teach and copolymerize so that the repeat unit shown by the general formula (1) may become more than 50 mol %. The method by the Wittig reaction is [among these] desirable in respect of control of a reaction, or yield.

[0023] The synthesis method of the arylene vinylene system copolymer which is one example of the macromolecule fluorescent substance used for the organic EL element of this invention is explained still more concretely. When obtaining a macromolecule fluorescent substance by the Wittig reaction for example, -- first -- a screw (halogenation methyl) compound -- more specifically 2 and 5-dioctyl oxy--p-KISHIRI range bromide For example, the inside of an N.N-dimethylformamide solvent, It is made to react with triphenyl phosphine and phosphonium salt is compounded. on this, a dialdehyde compound, and a twist concrete target For example, the macromolecule fluorescent substance containing a phenylenevinylene machine and a 2 and 5-dioctyl oxy--p-phenylenevinylene machine is obtained by the Wittig reaction which makes a terephthal aldehyde condense for example, among ethyl alcohol using lithium ethoxide. In order to obtain a copolymer, you may make two or more kinds of diphosphonium salts, and/or two or more kinds of dialdehyde compounds react at this time.

[0024] Since the purity affects a luminescence property when using these macromolecule fluorescent substances as a luminescent material of an organic EL element, it is desirable after composition to carry out purification processing of judgment by reprecipitation refining and the chromatograph etc.

[0025] Next, the protective layer used for the organic EL element of this invention is explained. It is isolated so that the organic EL element of this invention may be inserted with two transparent or translucent boards or film the interval from an anode plate front face or whose interval from a cathode surface is 100 micrometers or more 1mm or less preferably 1 micrometers or more 2mm or less and may not contact the open air. It is covered with the covering object which specifically consists of a joint which joins two transparent or translucent boards, a film and these two boards, or a film as this element, and the example isolated so that the open air may not be contacted is given. Since a crack may occur for an element when this element is directly joined to the both sides of two boards or a film, it is not desirable. Since glass, a polyethylene terephthalate (PET), a dampproof film, etc. are mentioned and glass and a dampproof film cannot penetrate the moisture in air, and oxygen easily as a material used for this board or a film, it is desirable.

[0026] The space between this element, this board, or a film, for example, the space between this element and this covering object, is filled with the inactive gas. As an inactive gas, nitrogen, an argon, helium, or a carbon dioxide is desirable, and an argon and nitrogen are still more desirable. In addition, the moisture content in an inactive gas has desirable 1000 ppm or less in order to prevent degradation of an element, and its 100 ppm or less are still more desirable.

[0027]

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[Means for Solving the Problem] The result wholeheartedly examined in order that this invention person etc. might see such a situation and might raise the luminous efficiency of the organic EL element using the macromolecule fluorescent substance as a luminous layer, In the organic EL element which has the luminous layer which consists of a poly arylene vinylene system macromolecule fluorescent substance By protecting an organic EL element by the inert gas, high brightness and the preservation property of the organic EL element of high luminous efficiency improved, and it found out that the organic electroluminescent element most does not generate and a dark spot does not grow up to be was obtained, and resulted in this invention.

[0008] That is, this invention is invention described below.

[1] In the organic electroluminescent element which has a luminous layer at least in inter-electrode [which at least one side becomes from the anode plate and cathode of a transparent or translucent couple] The macromolecule fluorescent substance with which this luminous layer has fluorescence by the solid state is included. this macromolecule fluorescent substance The repeat unit shown by the general formula (1) A 50 mol % not-less implication of all repeat units, the number average molecular weight of polystyrene conversion -- 103-107 it is -- this organic electroluminescent element Be caught with transparent or translucent the board or film the interval from an anode plate front face or whose interval from a cathode surface is two sheets it is [sheets] 1 micrometers or more 2mm or less. And it is the organic electroluminescent element which is isolated, becomes so that the open air may not be contacted, and the space between this element, this board, or a film is filled with an inactive gas, and is characterized by the bird clapper.

[Formula 2] -Ar-CR=CR'- (1)

(Here, Ar is the arylene machine or heterocyclic-compound machine with which the carbon atomic number which participates in conjugate combination consists of four or more pieces [20 or less], and R and R' shows the basis chosen from the group which consists of hydrogen, the alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, a heterocyclic compound of carbon numbers 4-20, and a cyano group independently, respectively.)

[0009] [2] Organic electroluminescent element given in [1] to which an inactive gas is characterized by being nitrogen, an argon, helium, or a carbon dioxide.

[3] Organic electroluminescent element given in [1] to which a board or a film is characterized by being the substrate of an anode plate or cathode.

[4] So that the organic electroluminescent element produced on the board transparent or translucent in an inactive gas or the film may be surrounded 1-micrometer or more spacer 2mm or less is placed on a transparent or translucent board or a film. Carry transparent or translucent an another board or an another film from besides, and a joint with a spacer, each two transparent or translucent boards, or a film is joined with an optical hardening type or heat-hardened type adhesives. The manufacture method of the organic electroluminescent element given in [1] characterized by light-hardening, or making this joint heat-harden, and joining two transparent or translucent boards or a film.

[0010] The organic EL element of this invention has at least the luminous layer which consists of an

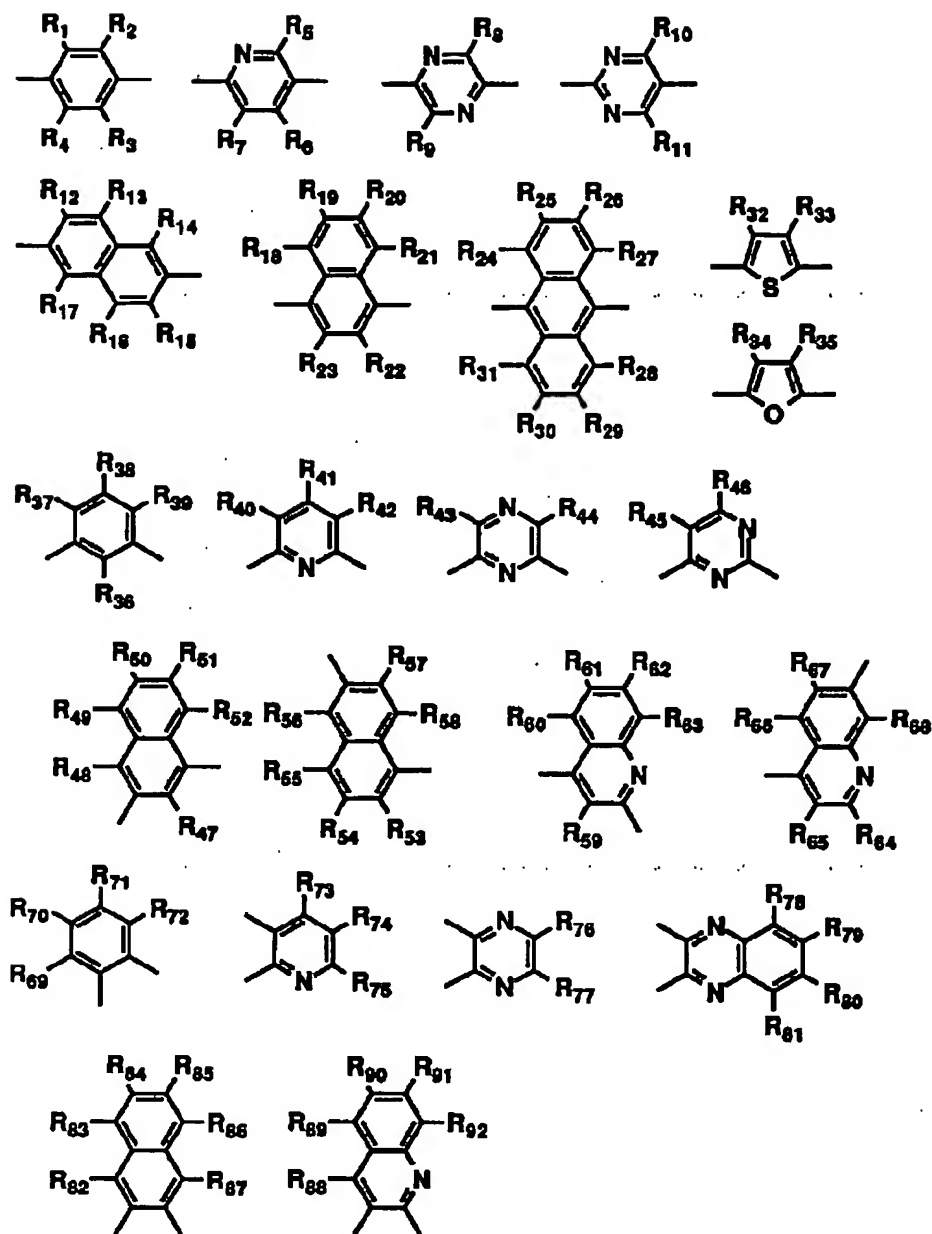
arylene vinylene system macromolecule fluorescent substance, and the inactive gas layer (it may be hereafter called a protective layer) which protects the aforementioned organic EL element.

[0011] The macromolecule fluorescent substance used for the luminous layer of the organic EL element of this invention is explained. the repeat unit this macromolecule fluorescent substance is indicated to be by the general formula (1) -- more than 50 mol % of all repeat units -- it is the included polymer. Although based also on the structure of a repeat unit, it is still more desirable that the repeat units shown by the general formula (1) are 70% or more of all repeat units. This macromolecule fluorescent substance may contain a divalent aromatic compound machine or its derivative, a divalent heterocyclic-compound machine, its derivative, or the basis obtained combining them as repeat units other than the repeat unit shown by the general formula (1). Moreover, the repeat unit shown by the general formula (1) and other repeat units may be connected in the disconjugation unit which has an ether machine, an ester machine, an amide group, an imido basis, etc., and those disconjugation portions may be contained per repeat.

[0012] The carbon atomic number which participates in conjugate combination as Ar of a general formula (1) in the macromolecule fluorescent substance in this invention is the arylene machine or heterocyclic-compound machine which consists of four or more pieces [20 or less], and the divalent aromatic compound machine shown below, the derivative machine and a divalent heterocyclic-compound machine, its derivative machine, or the basis obtained combining them is illustrated.

[0013]

[Formula 3]



(R₁ -R₉₂ are the basis independently chosen from the group which becomes hydrogen, the alkyl group of carbon numbers 1-20, an alkoxy group, the aryl group of the alkyl thio basis; carbon numbers 6-18, and an aryloxy group; row from the heterocyclic-compound machine of carbon numbers 4-14, respectively.)

[0014] A phenylene group, a substitution phenylene group, a biphenylene machine, a substitution biphenylene machine, a naphthalene diyl machine, a substitution naphthalene diyl machine, an anthracene -9, 10-diyl machine, the substitution anthracene -9, 10-diyl machine, a pyridine -2, 5-diyl machine, the substitution pyridine -2, 5-diyl machine, a thienylene machine, and a substitution thienylene machine are desirable in these. They are a phenylene group, a biphenylene machine, a naphthalene diyl machine, a pyridine -2, 5-diyl machine, and a thienylene machine still more preferably.

[0015] R of a general formula (1) and R' show the basis chosen from the group which consists of hydrogen, the alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, a heterocyclic compound of carbon numbers 4-20, and a cyano group independently, respectively. As an alkyl group of carbon numbers 1-20, a methyl group, an ethyl group, a propyl group, a butyl, a pentyl

machine, a hexyl machine, a heptyl machine, an octyl machine, a decyl group, a lauryl machine, etc. are mentioned, and a methyl group, an ethyl group, a pentyl machine, a hexyl machine, a heptyl machine, and an octyl machine are desirable. As an aryl group, a phenyl group, a 4-C1 - C12 alkoxy phenyl group (C1 -C12 show that a carbon number is the number of either 1-12.), 4-C1 - C12 alkylphenyl machine, 1-naphthyl group, 2-naphthyl group, etc. are illustrated.

[0016] It is desirable that Ar of a general formula (1) has one or more bases chosen as the alkyl group of carbon numbers 4-20, the alkoxy group and the alkyl thio machine, the aryl group of carbon numbers 6-18, and the aryloxy group row from the heterocyclic-compound machine of carbon numbers 4-14 from a viewpoint of solvent fusibility.

[0017] Specifically, as an alkyl group of carbon numbers 4-20, a butyl, a pentyl machine, a hexyl machine, a heptyl machine, an octyl machine, a decyl group, a lauryl machine, etc. are mentioned, and a pentyl machine, a hexyl machine, a heptyl machine, and an octyl machine are desirable. Moreover, as an alkoxy group of carbon numbers 4-20, a butoxy machine, a pentyloxy machine, a hexyloxy machine, a heptyloxy machine, an octyloxy machine, a decyloxy machine, a lauryl oxy-basis, etc. are mentioned, and a pentyloxy machine, a hexyloxy machine, a heptyloxy machine, and an octyloxy machine are desirable. As an alkyl thio machine, a butyl thio machine, a pentyl thio machine, a hexyl thio machine, a heptyl thio machine, an octyl thio machine, a decyloxy machine, a laurylthio machine, etc. are mentioned, and a pentyl thio machine, a hexyl thio machine, a heptyl thio machine, and an octyl thio machine are desirable. As an aryl group, a phenyl group, a 4-C1 - C12 alkoxy phenyl group, 4-C1 - C12 alkylphenyl machine, 1-naphthyl group, 2-naphthyl group, etc. are illustrated. A phenoxy machine is illustrated as an aryloxy group. As a heterocyclic-compound machine, 2-thienyl group, 2-pyrrolyl machine, 2-furyl machine, 2-, 3-, or 4-pyridyl machine is illustrated. Although the number of these substituents differs from the molecular weight of this macromolecule fluorescent substance also by composition of a unit repeatedly, it is desirable that the viewpoint which obtains a soluble high macromolecule fluorescent substance to these substituents are one or more per molecular weight 600.

[0018] In addition, the macromolecule fluorescent substance used for the organic EL element of this invention may be randomness, a block, or a graft copolymer, and may be the macromolecule which has those middle-structures, for example, the random copolymer which wore block nature. From a viewpoint which obtains the high macromolecule fluorescent substance of the quantum yield of fluorescence, a random copolymer, and the block or graft copolymer which wore block nature is more desirable than a perfect random copolymer. Moreover, since the organic EL element of this invention uses luminescence from a thin film, that in which this macromolecule fluorescent substance has fluorescence by the solid state is used.

[0019] As a good solvent to this macromolecule fluorescent substance, chloroform, a methylene chloride, a dichloroethane, a tetrahydrofuran, toluene, a xylene, etc. are illustrated. although based also on the structure and molecular weight of a macromolecule fluorescent substance -- usually -- these solvents -- more than 0.1wt% -- it can be made to dissolve

[0020] The molecular weight of the macromolecule fluorescent substance in this invention is 103-107 in polystyrene conversion, and those polymerization degree changes also with repeat structure or its rate. general [from the point of membrane formation nature] -- the total number of repeat structure -- desirable -- 4-10000 -- further -- desirable -- 5-3000 -- it is 10-2000 especially preferably

[0021] When forming membranes from a solution by using the macromolecule fluorescent substance of such organic-solvent fusibility, in the case of organic EL-element creation, when [which mentions this solution later that what is necessary is just for the dryness after an application to remove a solvent] charge transportation material and luminescent material are mixed further, the same technique can be applied, and it is very advantageous to it on manufacture.

[0022] Although not limited especially as a synthesis method of the macromolecule fluorescent substance used for the organic EL element of this invention, the Wittig reaction from the diphosphonium salt obtained from the dialdehyde compound which two aldehyde groups combined with the arylene machine, the compound which two halogenation methyl groups combined with the arylene machine, and triphenyl phosphine, for example is illustrated. Moreover, as other synthesis methods, the

dehydrohalogenation method from the compound which two halogenation methyl groups combined with the arylene machine is illustrated. Furthermore, the sulfonium salinity solution method which obtains this macromolecule fluorescent substance from the intermediate field obtained by carrying out the polymerization of the sulfonium salt of the compound which two halogenation methyl groups combined with the arylene machine with alkali with heat treatment is illustrated. Since the structure of the repeat unit included in the macromolecule fluorescent substance generated by adding as a monomer the compound which has skeletons other than an arylene machine also in which synthesis method, and changing the abundance is changeable, you may adjust, teach and copolymerize so that the repeat unit shown by the general formula (1) may become more than 50 mol %. The method by the Wittig reaction is [among these] desirable in respect of control of a reaction, or yield.

[0023] The synthesis method of the arylene vinylene system copolymer which is one example of the macromolecule fluorescent substance used for the organic EL element of this invention is explained still more concretely. When obtaining a macromolecule fluorescent substance by the Wittig reaction for example, -- first -- a screw (halogenation methyl) compound -- more specifically 2 and 5-dioctyl oxy--p-KISHIRI range bromide For example, the inside of an N.N-dimethylformamide solvent, It is made to react with triphenyl phosphine and phosphonium salt is compounded. on this, a dialdehyde compound, and a twist concrete target For example, the macromolecule fluorescent substance containing a phenylenevinylene machine and a 2 and 5-dioctyl oxy--p-phenylenevinylene machine is obtained by the Wittig reaction which makes a terephthal aldehyde condense for example, among ethyl alcohol using lithium ethoxide. In order to obtain a copolymer, you may make two or more kinds of diphosphonium salts, and/or two or more kinds of dialdehyde compounds react at this time.

[0024] Since the purity affects a luminescence property when using these macromolecule fluorescent substances as a luminescent material of an organic EL element, it is desirable after composition to carry out purification processing of judgment by reprecipitation refining and the chromatograph etc.

[0025] Next, the protective layer used for the organic EL element of this invention is explained. It is isolated so that the organic EL element of this invention may be inserted with two transparent or translucent boards or film the interval from an anode plate front face or whose interval from a cathode surface is 100 micrometers or more 1mm or less preferably 1 micrometers or more 2mm or less and may not contact the open air. It is covered with the covering object which specifically consists of a joint which joins two transparent or translucent boards, a film and these two boards, or a film as this element, and the example isolated so that the open air may not be contacted is given. Since a crack may occur for an element when this element is directly joined to the both sides of two boards or a film, it is not desirable. Since glass, a polyethylene terephthalate (PET), a dampproof film, etc. are mentioned and glass and a dampproof film cannot penetrate the moisture in air, and oxygen easily as a material used for this board or a film, it is desirable.

[0026] The space between this element, this board, or a film, for example, the space between this element and this covering object, is filled with the inactive gas. As an inactive gas, nitrogen, an argon, helium, or a carbon dioxide is desirable, and an argon and nitrogen are still more desirable. In addition, the moisture content in an inactive gas has desirable 1000 ppm or less in order to prevent degradation of an element, and its 100 ppm or less are still more desirable.

[0027] About the structure of the organic EL element of this invention, the above-mentioned macromolecule fluorescent substance is used into the luminous layer which at least one side prepares in inter-electrode [of a transparent or translucent couple]. as a protective layer Since it is isolated so that the open air may not be contacted in this organic EL element, if it is covered with two transparent or translucent boards or film separated in 1-micrometer or more space 2mm or less filled with the inactive gas, there will be especially no limit and well-known structure will be adopted. For example, the thing of structure which has the electrode of a couple to both sides of the luminous layer which consists of this macromolecule fluorescent substance, or the luminous layer which consists of mixture of this macromolecule fluorescent substance and charge transportation material (the general term of electronic transportation material and electron hole transportation material is meant), What carried out the laminating of the electron hole transporting bed which contains electron hole transportation material

between a luminous layer and an anode plate, What carried out the laminating of the electronic transporting bed which carries out the laminating of what carried out the laminating of the electronic transporting bed which contains electronic transportation material between a luminous layer and cathode, and the electron hole transporting bed which contains electron hole transportation material between a luminous layer and an anode plate further, and contains electronic transportation material between a luminous layer and cathode is illustrated. Moreover, about a luminous layer or a charge transporting bed, the case of one layer, and when combining two or more layers, it is contained in this invention. Furthermore, you may carry out mixed use of the luminescent material stated to a luminous layer at the following for example, other than this macromolecule fluorescent substance. Moreover, it can also consider as the layer which made the high molecular compound distribute this macromolecule fluorescent substance and/or charge transportation material.

[0028] the charge transportation material used with the macromolecule fluorescent substance of this invention -- that is Although a thing well-known as electronic transportation material or an electron hole transportation material can be used and it is not limited especially As an electron hole transportation material, a pyrazoline derivative, an arylamine derivative, a stilbene derivative, A triphenyl diamine derivative etc. as an electronic transportation material An OKISA diazole derivative, An anthra quinodimethan and its derivative, a benzoquinone, and its derivative, A naphthoquinone and its derivative, anthraquinone, and its derivative, a tetracyano ANSURA quinodimethan and its derivative, and full -- me -- non, the metal complex of a derivative, diphenyl dicyano ethylene and its derivative, a diphenoquinone derivative, 8-hydroxyquinoline, and its derivative etc. is illustrated

[0029] Specifically, what is indicated by JP,63-70257,A, a 63-175860 official report, JP,2-135359,A, 2-135361, 2-209988, 3-37992, and the 3-152184 official report is illustrated. As an electron hole transportation material, as a triphenyl diamine derivative and an electronic transportation material, an OKISA diazole derivative, A benzoquinone and its derivative, anthraquinone, and its derivative, The metal complex of 8-hydroxyquinoline and its derivative is desirable. especially As an electron hole transportation material, a 4 and 4'-screw (N(3-methylphenyl)-N-phenylamino) biphenyl, as electronic transportation material -- 2-(4-biphenyl)-5-(4-t-butylphenyl)- 1, 3, 4-OKISA diazole, a benzoquinone, anthraquinone, and tris (eight quinolinol) aluminum are desirable What is necessary is just to use simultaneously the compound of electronic transportability, the compound of electron hole transportability, or both among these. These may be used independently, and may mix and use two or more kinds.

[0030] What is necessary is just to form a charge transporting bed using such charge transportation material, when preparing a charge transporting bed further between a luminous layer and an electrode. Moreover, what is necessary is just to decide suitably in consideration of them in the range which does not check sufficient membrane formation nature and a luminescence property, since the amount of the charge transportation material used changes with kinds of compound to be used etc. when mixing and using charge transportation material for a luminous layer. Usually, it is 1 - 40 % of the weight to luminescent material, and is 2 - 30 % of the weight still more preferably.

[0031] Although not limited especially as a well-known luminescent material which can be used with the macromolecule fluorescent substance in this invention, coloring matter, such as a naphthalene derivative, an anthracene and its derivative, a perylene and its derivative, a poly methine system, a xanthene system, a coumarin system, and a cyanine system, 8-hydroxyquinoline and the metal complex of the derivative, an aromatic amine, a tetrapod phenyl cyclopentadiene and its derivative, a tetrapod phenyl butadiene, its derivative, etc. can be used, for example. Specifically, what is indicated by JP,57-51781,A and the 59-194393 official report is usable.

[0032] Next, the typical production method of an organic EL element using the luminescent material of this invention is described based on drawing 1 . In addition, about the pattern of an anode plate and cathode, since a well-known pattern can be used, the detail of the pattern is omitted by drawing 1 . Moreover, in drawing 1 , when one sheet of two transparent or translucent boards or a film serves as the substrate of an anode plate, it corresponds. What formed the transparent or translucent electrode as an anode plate 4 on transparent or translucent a board or films 1, such as glass and transparent plastics, is

used. As a material of an anode plate 4, a conductive metallic-oxide film, a translucent metal thin film, etc. are used. The films (NESA etc.) created using the electrically conductive glass which specifically consists of indium tin oxide (ITO), tin oxide, etc., gold, platinum, silver, copper, etc. are used. As the production method, a vacuum deposition method, the sputtering method, plating, etc. are used. The thing same also as cathode 8 is used.

[0033] On this anode plate 4, the luminous layer 6 which contains the above-mentioned macromolecule fluorescent substance or this macromolecule fluorescent substance, and charge transportation material as a luminescent material is formed. Although the applying methods, such as the spin coating method, the casting method, a dipping method, the bar coat method, and the roll coat method, are illustrated as the formation method using the melting liquid, solution, or mixed liquor of these material, especially the thing to form using a solution or mixed liquor is desirable.

[0034] 1nm - 1 micrometer is 2nm - 500nm still more preferably preferably as thickness of a luminous layer 6. In order to raise current density and to gather luminous efficiency, the range of 5-200nm is desirable. In addition, when a luminous layer 6 is thin-film-ized by the applying method, in order to remove a solvent, it is desirable to carry out stoving of the 30-300 degrees C at the temperature of 60-200 degrees C preferably under reduced pressure or an inert atmosphere after luminous layer formation.

[0035] When carrying out the laminating of the electron hole transporting bed 5 to the bottom of this luminous layer 6, before forming a luminous layer 6 by the above-mentioned membrane formation method (when shown in drawing 1), it is desirable to form the electron hole transporting bed 5. Although not limited, especially as the membrane formation method of the electron hole transporting bed 5 The vacuum deposition method from a powder state, Or the spin coating method after melting in a solution, the casting method, The applying methods, such as a dipping method, the bar coat method, and the roll coat method, or the spin coating method after mixing a high molecular compound and charge transportation material in the state of a solution state or melting and making it distribute; The applying methods, such as the casting method, a dipping method, the bar coat method, and the roll coat method, can be used.

[0036] Especially as a high molecular compound to mix, although not limited, what has the absorption desirable what does not check charge transportation to a degree very much and not strong to the light is used suitably. For example, poly (N-vinylcarbazole), the poly aniline and its derivative, the poly thiophene and its derivative, poly (p-phenylenevinylene) and its derivative, poly (2, 5-thienylene vinylene) and its derivative, a polycarbonate, a polyacrylate, poly methyl acrylate, a polymethylmethacrylate, polystyrene, a polyvinyl chloride, a polysiloxane, etc. are illustrated. When using a high molecular compound in that membranes can be formed easily, it is desirable to use the applying method.

[0037] Although thickness which a pinhole does not generate at least is required for it, if the thickness of the electron hole transporting bed 5 is not much thick, resistance of an element increases and its high driver voltage is not needed and desirable. Therefore, 1nm - 1 micrometer of 2nm - 500nm of thickness of a charge transporting bed is 5-200nm especially preferably still more preferably preferably.

[0038] Moreover, when carrying out the laminating of the electronic transporting bed 7 further on this luminous layer, after forming a luminous layer 6 by the above-mentioned membrane formation method (when shown in drawing 1), it is desirable to form the electronic transporting bed 7 on it.

[0039] Although not limited, especially as the membrane formation method of the electronic transporting bed 7 The vacuum deposition method from a powder state, Or the spin coating method after melting in a solution, the casting method, The applying methods, such as a dipping method, the bar coat method, and the roll coat method, or the spin coating method after mixing a high molecular compound and charge transportation material in the state of a solution state or melting and making it distribute, The applying methods, such as the casting method, a dipping method, the bar coat method, and the roll coat method, can be used.

[0040] Especially as a high molecular compound to mix, although not limited, what has the absorption desirable what does not check charge transportation to a degree very much and not strong to the light is used suitably. For example, poly (N-vinylcarbazole), the poly aniline and its derivative, the poly

thiophene and its derivative, poly (p-phenylenevinylene) and its derivative, poly (2, 5-thienylene vinylene) and its derivative, a polycarbonate, a polyacrylate, poly methyl acrylate, a polymethylmethacrylate, polystyrene, a polyvinyl chloride, a polysiloxane, etc. are illustrated. When using a high molecular compound in that membranes can be formed easily, it is desirable to use the applying method. Although thickness which a pinhole does not generate at least is required for it, if the thickness of the electronic transporting bed 7 is not much thick, resistance of an element increases and its high driver voltage is not needed and desirable. Therefore, 1nm - 1 micrometer of 2nm - 500nm of thickness of a charge transporting bed is 5-200nm especially preferably still more preferably preferably. [0041] Subsequently, cathode 8 is formed on a luminous layer 6 or the electronic transporting bed 7. This cathode 8 turns into electron-injection cathode. Especially as the material, although not limited, a small material of ionization energy is desirable. For example, aluminum, an indium, magnesium, calcium, a lithium, a magnesium-silver alloy, a magnesium-indium alloy, a magnesium-indium alloy, a lithium-aluminium alloy, a lithium-silver alloy, a lithium-indium alloy, or a graphite thin film is used. A vacuum deposition method, the sputtering method, etc. are used as the production method of cathode. [0042] Next, one example of the manufacture method of the protective layer of the organic EL element in this invention is explained based on drawing 1. By performing the following operations in an inactive gas, the space between this organic EL element, a transparent or translucent board, or a film, i.e., the space between this organic EL element and a covering object, is filled with the inactive gas 9. First, the 1-micrometer or more spacer 3 2mm or less is placed on a transparent or translucent board or a film 1 (it serves as a substrate.), and transparent or translucent another board or another film 10 is carried from this so that the organic electroluminescent element produced on the board transparent as mentioned above or translucent or the film 1 (it serves as a substrate.) may be surrounded. Next, a joint with a spacer 3, each two transparent or translucent boards, or a film is joined with an optical hardening type or the heat-hardened type adhesives 2, light-harden, or this joint is made to heat-harden, and two transparent or translucent boards or a film is joined. Thereby, an organic EL element is intercepted with the open air.

[0043]

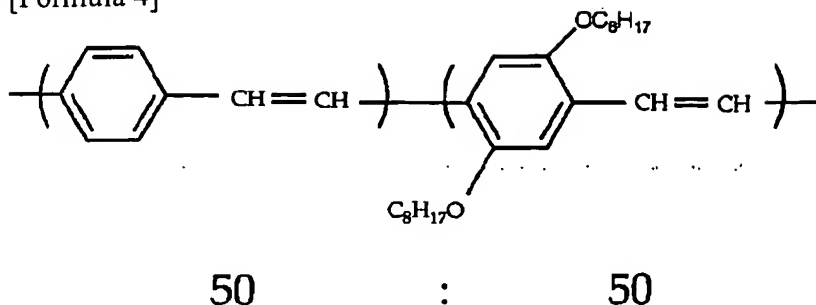
[Function] Since the melting point and the decomposition temperature use comparatively high polymeric materials, it is thermally stable that the organic EL element of this invention is excellent, and it is because a luminous layer can be easily formed by the applying method. For this reason, high brightness and the organic EL element of high luminous efficiency can be produced very easily. Furthermore, it is thought that it is effective in reinforcement being possible since especially the endurance of cathode is high, and suppressing generation of a dark spot by operation of the protective layer used by this invention.

[0044]

[Example] Hereafter, although the example of this invention is shown, this invention is not limited to these. Here, about number average molecular weight, the number average molecular weight of polystyrene conversion was calculated by the gel permeation chromatography (GPC) by using chloroform as a solvent.

Example 1 <composition of macromolecule fluorescent substance 1> 2 and 5-dioctyl oxy--p-KISHIRI range bromide was made to react with the inside of an N.N-dimethylformamide solvent, and triphenyl phosphine, and phosphonium salt was compounded. The obtained phosphonium salt 47.75 weight section and the terephthal aldehyde 6.7 weight section were dissolved in ethyl alcohol. The ethyl alcohol solution containing the lithium ethoxide of the 5.8 weight sections was dropped at the ethyl alcohol solution of phosphonium salt and a dialdehyde, and the polymerization was carried out at the room temperature for 3 hours. After leaving it at an overnight room temperature, precipitation was carried out the ** exception, with ethyl alcohol, the dissolution was added to chloroform after washing, ethanol was added to this, and reprecipitation generation was carried out. Reduced pressure drying of this was carried out, and the polymer 8.0 weight section was obtained. This is called macromolecule fluorescent substance 1. The repeat unit and mole ratio of the macromolecule fluorescent substance 1 calculated from the preparation ratio of a monomer are shown below.

[Formula 4]



Here, two repeat units are combined by turns. the number average molecular weight of polystyrene conversion of this macromolecule fluorescent substance 1 -- 1.0×10^4 it was . About the structure of this macromolecule fluorescent substance 1, it checked by the infrared absorption spectrum and NMR.

[0045] By creation of an element, and <evaluation> sputtering, the 1.0wt% chloroform solution of a polyvinyl carbazole was used for the glass substrate which attached the ITO film by the thickness of 40nm, and membranes were formed by the thickness of 50nm by dipping. Furthermore, membranes were formed by the thickness of 50nm with the spin coat using the 1.0wt% toluene solution of the macromolecule fluorescent substance 1. Furthermore, after drying this at 150 degrees C under reduced pressure for 1 hour, 35nm (Alq3) of tris (eight quinolinol) aluminum was deposited at the rate of 0.1 - 0.2 nm/s as an electronic transporting bed. 40nm vacuum evaporation of the lithium-aluminium alloy (lithium concentration : 1wt%) was carried out as 1st metal layer of cathode on it, and the organic EL element was produced. All the degree of vacuums at the time of vacuum evaporation were 8×10^{-6} or less Torr. After electrode production, the spacer of 1mm glass was put on the circumference of the organic EL element produced on the transparent substrate in nitrogen-gas-atmosphere mind, the glass plate was carried from on this, and the organic EL-element protective layer was produced by pasting up a substrate and this glass plate for the spacer section using optical hardening type adhesives. When voltage 12.5V are impressed to this element, the current of 2 flows the current density of 32.1mA/cm, and it is brightness 1892 cd/m². Yellow-green EL luminescence was observed. The luminous efficiency at this time was 5.9 cd/A. Brightness was proportional to current density mostly. Moreover, EL peak wavelength was 540nm, simultaneously coincidence is carried out with the fluorescence peak wavelength of the thin film of the macromolecule fluorescent substance 1, and EL luminescence [fluorescent substance / macromolecule / 1] was checked. When the low-battery drive of this element was carried out by 10V after preservation for five days in air, there was little generating of a dark spot and the area for a non-light-emitting part was 10% or less.

[0046] The element was created by the same method as an example 1 except not using the protective layer of an example of comparison 1 organic EL element. When voltage 12.5V were impressed to this element, it is 2 the current density of 32.1mA/cm. Current flows and it is brightness 1892 cd/m². Yellow-green EL luminescence was observed. The luminous efficiency at this time was 5.9 cd/A. Brightness was proportional to current density mostly. Moreover, EL peak wavelength was 540nm, simultaneously coincidence is carried out with the fluorescence peak wavelength of the thin film of the macromolecule fluorescent substance 1, and EL luminescence [fluorescent substance / macromolecule / 1] was checked. When the low-battery drive of this element was carried out by 10V after preservation for five days in air, there was much generating of a dark spot and the area for a non-light-emitting part was about about 50%.

[0047] Thus, rather than the organic EL element of the example 1 of comparison which is not covered by the glass plate of two sheets separated in the 1mm space filled with the inactive gas, the organic EL element covered by the glass plate of two sheets separated in the 1mm space where the organic EL element of an example 1 was filled with the inactive gas had little generating of a dark spot, and showed the preservation property of the outstanding luminescence display grace.

[0048]

[Effect of the Invention] The space [2mm or less] 1 micrometers or more filled with the inactive gas in the macromolecule fluorescent substance and cathode of this invention and the organic electroluminescent element isolated so that the open air may not be contacted with wrap covering in them are easy to create, and since the preservation property of the outstanding luminescence display grace is shown, it can be preferably used as equipments, such as the field-like light source as a back light, and a flat-panel display.

[Translation done.]

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TECHNICAL FIELD

[Industrial Application] this invention relates to the organic electroluminescent element (it may be hereafter called an organic EL element) which used the macromolecule fluorescent substance, and its manufacture method.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] The inorganic electroluminescent element (it may be hereafter called an inorganic EL element) using the inorganic fluorescent substance as a luminescent material needed the alternating current of the high voltage for making light emit, although used for display, such as the field-like light source as a back light, and a flat-panel display. In recent years, the organic EL element which has the two-layer structure which Tang and others made the organic fluorochrome the luminous layer, and carried out the laminating of this and the organic charge transportation compound used for the photo conductor of electrophotography etc. was produced (JP,59-194393,A). An organic EL element is [Japanese journal OBU applied physics to which many attempts are reported about element structure, the organic fluorochrome, and the organic charge transportation compound since there is the feature that luminescence of many colors is obtained easily in addition to a low-battery drive and high brightness, compared with an inorganic EL element. (Jpn.J.Appl.Phys.) The 27th volume of L 269 pages (1988) and the 65th volume (J. Appl.Phys.) of journal OBU applied physics, 3610page(1989)].

[0003] until now, generally as a material used for a luminous layer, the organic fluorochrome of low molecular weight uses -- having -- **** -- as the luminescent material of the amount of macromolecules -- WO No. 9013148 public presentation specification, JP,3-244630,A, and applied physics Letters (Appl.Phys.Lett.) -- it was proposed by the 58th volume, 1982 etc. pages (1991), etc. A fusibility precursor is formed on an electrode, the poly (p-phenylenevinylene) thin film changed into the conjugated-system macromolecule by heat-treating is obtained by the example of WO No. 9013148 public presentation specification, and the EL element using it is indicated. Moreover, itself is meltable to a solvent and the conjugated-system macromolecule which has the feature that heat treatment is unnecessary is illustrated by JP,3-244630,A. applied physics Letters (Appl.Phys.Lett.) -- the organic EL element created at the solvent using a meltable macromolecule luminescent material and meltable it to the 58th volume and no less than 1982 pages (1991) is indicated. However, the low defect of brightness in which luminous efficiency was called dark spot during preservation highly not necessarily enough arose in the luminescence side, and the organic EL element created using such material was reducing display grace.

[0004] About the organic EL element using the low-molecular organic fluorochrome, the organic EL element which used for the metallic material of cathode liquid material, such as independent material or the solid material by which vapor codeposition was carried out, such as an indium and an aluminum quinolinol complex, a silicone oil, and fluorination carbon, as a protective layer of an electrode as a protective layer is indicated by JP,5-101892,A, 159881, and the No. 129080 or 41281 official report.

[0005] However, in the organic EL element using the macromolecule reported until now, during preservation, the low defect of the brightness called dark spot to an element arose in the luminescence side, and improvement in display quality, fall prevention of the display grace at the time of preservation, generation of a dark spot, and suppression of growth were called for. In order that the method conventionally used in order to suppress a dark spot might contact a solid-state and a liquid to an electrode, we were anxious about degradation by diffusion of the defect by generating of a blemish, and an impurity etc. Moreover, by carrying out the vacuum evaporation of the expensive material etc., it

could not become a manufacture process in a low cost.

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EFFECT OF THE INVENTION

[Effect of the Invention] The space [2mm or less] 1 micrometers or more filled with the inactive gas in the macromolecule fluorescent substance and cathode of this invention and the organic electroluminescent element isolated so that the open air may not be contacted with wrap covering in them are easy to create, and since the preservation property of the outstanding luminescence display grace is shown, it can be preferably used as equipments, such as the field-like light source as a back light, and a flat-panel display.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The purposes of this invention are the high brightness and high luminous efficiency which used the macromolecule, and the organic EL element of low driver voltage, and are to offer cheaply the organic electroluminescent element also set to long-term preservation, and a dark spot hardly generates and grows up to be.

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MEANS

[Means for Solving the Problem] The result wholeheartedly examined in order that this invention person etc. might see such a situation and might raise the luminous efficiency of the organic EL element using the macromolecule fluorescent substance as a luminous layer, In the organic EL element which has the luminous layer which consists of a poly arylene vinylene system macromolecule fluorescent substance By protecting an organic EL element by the inert gas, high brightness and the preservation property of the organic EL element of high luminous efficiency improved, and it found out that the organic electroluminescent element most does not generate and a dark spot does not grow up to be was obtained, and resulted in this invention.

[0008] That is, this invention is invention described below.

[1] In the organic electroluminescent element which has a luminous layer at least in inter-electrode [which at least one side becomes from the anode plate and cathode of a transparent or translucent couple] The macromolecule fluorescent substance with which this luminous layer has fluorescence by the solid state is included. this macromolecule fluorescent substance The repeat unit shown by the general formula (1) A 50 mol % not-less implication of all repeat units, the number average molecular weight of polystyrene conversion -- 103-107 it is -- this organic electroluminescent element Be caught with transparent or translucent the board or film the interval from an anode plate front face or whose interval from a cathode surface is two sheets it is [sheets] 1 micrometers or more 2mm or less. And it is the organic electroluminescent element which is isolated, becomes so that the open air may not be contacted, and the space between this element, this board, or a film is filled with an inactive gas, and is characterized by the bird clapper.

[Formula 2] $-\text{Ar}-\text{CR}=\text{CR}'-$ (1)

(Here, Ar is the arylene machine or heterocyclic-compound machine with which the carbon atomic number which participates in conjugate combination consists of four or more pieces [20 or less], and R and R' shows the basis chosen from the group which consists of hydrogen, the alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, a heterocyclic compound of carbon numbers 4-20, and a cyano group independently, respectively.)

[0009] [2] Organic electroluminescent element given in [1] to which an inactive gas is characterized by being nitrogen, an argon, helium, or a carbon dioxide.

[3] Organic electroluminescent element given in [1] to which a board or a film is characterized by being the substrate of an anode plate or cathode.

[4] So that the organic electroluminescent element produced on the board transparent or translucent in an inactive gas or the film may be surrounded 1-micrometer or more spacer 2mm or less is placed on a transparent or translucent board or a film. Carry transparent or translucent an another board or an another film from besides, and a joint with a spacer, each two transparent or translucent boards, or a film is joined with an optical hardening type or heat-hardened type adhesives. The manufacture method of the organic electroluminescent element given in [1] characterized by light-hardening, or making this joint heat-harden, and joining two transparent or translucent boards or a film.

[0010] The organic EL element of this invention has at least the luminous layer which consists of an

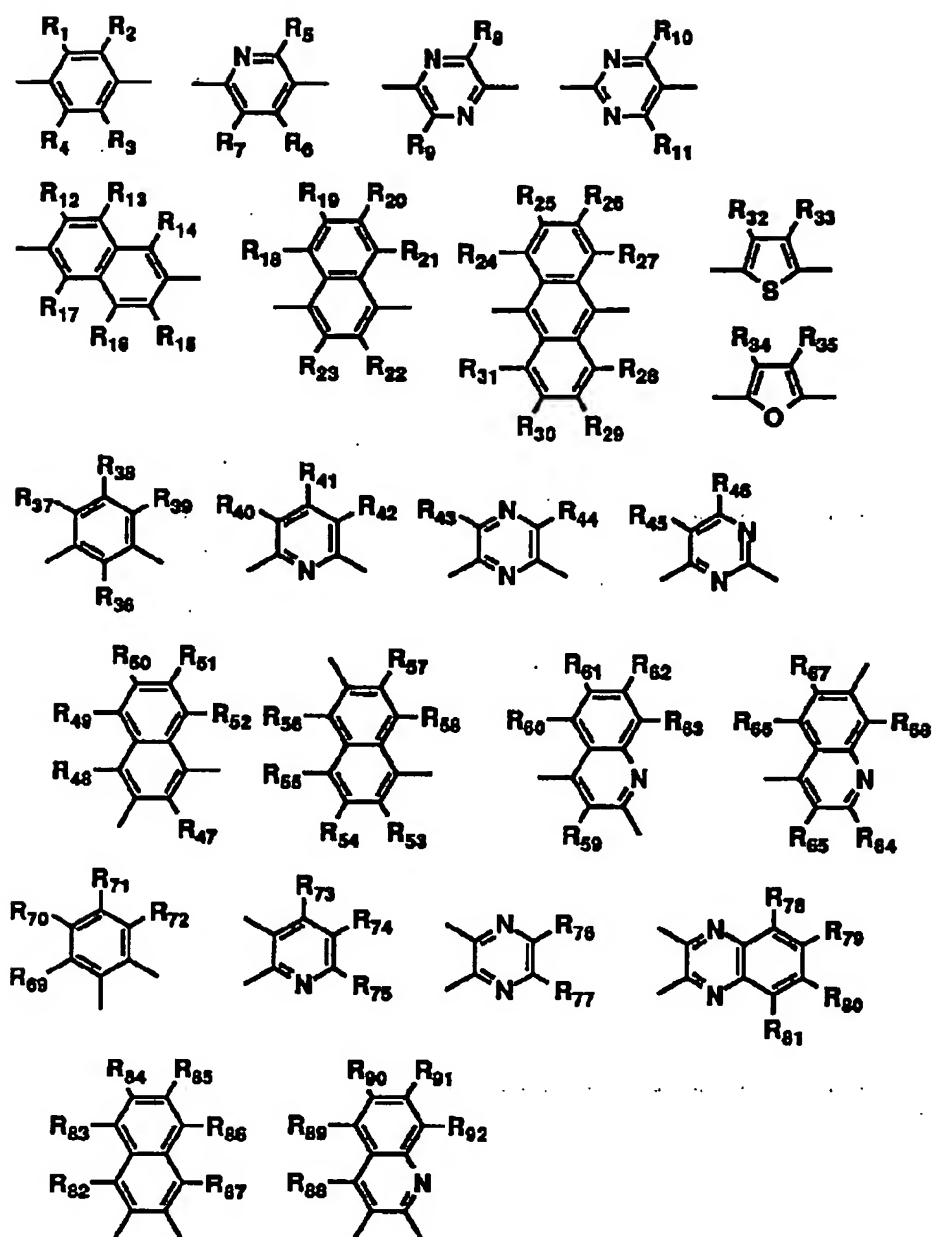
arylene vinylene system macromolecule fluorescent substance, and the inactive gas layer (it may be hereafter called a protective layer) which protects the aforementioned organic EL element.

[0011] The macromolecule fluorescent substance used for the luminous layer of the organic EL element of this invention is explained. the repeat unit this macromolecule fluorescent substance is indicated to be by the general formula (1) -- more than 50 mol % of all repeat units -- it is the included polymer. Although based also on the structure of a repeat unit, it is still more desirable that the repeat units shown by the general formula (1) are 70% or more of all repeat units. This macromolecule fluorescent substance may contain a divalent aromatic compound machine or its derivative, a divalent heterocyclic-compound machine, its derivative, or the basis obtained combining them as repeat units other than the repeat unit shown by the general formula (1). Moreover, the repeat unit shown by the general formula (1) and other repeat units may be connected in the disconjugation unit which has an ether machine, an ester machine, an amide group, an imido basis, etc., and those disconjugation portions may be contained per repeat.

[0012] The carbon atomic number which participates in conjugate combination as Ar of a general formula (1) in the macromolecule fluorescent substance in this invention is the arylene machine or heterocyclic-compound machine which consists of four or more pieces [20 or less], and the divalent aromatic compound machine shown below, the derivative machine and a divalent heterocyclic-compound machine, its derivative machine, or the basis obtained combining them is illustrated.

[0013]

[Formula 3]



(R1 -R92 are the basis independently chosen from the group which becomes hydrogen, the alkyl group of carbon numbers 1-20, an alkoxy group, the aryl group of the alkyl thio basis; carbon numbers 6-18, and an aryloxy group; row from the heterocyclic-compound machine of carbon numbers 4-14, respectively.)

[0014] A phenylene group, a substitution phenylene group, a biphenylene machine, a substitution biphenylene machine, a naphthalene diyl machine, a substitution naphthalene diyl machine, an anthracene -9, 10-diyl machine, the substitution anthracene -9, 10-diyl machine, a pyridine -2, 5-diyl machine, the substitution pyridine -2, 5-diyl machine, a thienylene machine, and a substitution thienylene machine are desirable in these. They are a phenylene group, a biphenylene machine, a naphthalene diyl machine, a pyridine -2, 5-diyl machine, and a thienylene machine still more preferably.

[0015] R of a general formula (1) and R' show the basis chosen from the group which consists of hydrogen, the alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, a heterocyclic compound of carbon numbers 4-20, and a cyano group independently, respectively. As an alkyl group of carbon numbers 1-20, a methyl group, an ethyl group, a propyl group, a butyl, a pentyl

machine, a hexyl machine, a heptyl machine, an octyl machine, a decyl group, a lauryl machine, etc. are mentioned, and a methyl group, an ethyl group, a pentyl machine, a hexyl machine, a heptyl machine, and an octyl machine are desirable. As an aryl group, a phenyl group, a 4-C1 - C12 alkoxy phenyl group (C1 -C12 show that a carbon number is the number of either 1-12.), 4-C1 - C12 alkylphenyl machine, 1-naphthyl group, 2-naphthyl group, etc. are illustrated.

[0016] It is desirable that Ar of a general formula (1) has one or more bases chosen as the alkyl group of carbon numbers 4-20, the alkoxy group and the alkyl thio machine, the aryl group of carbon numbers 6-18, and the aryloxy group row from the heterocyclic-compound machine of carbon numbers 4-14 from a viewpoint of solvent fusibility.

[0017] Specifically, as an alkyl group of carbon numbers 4-20, a butyl, a pentyl machine, a hexyl machine, a heptyl machine, an octyl machine, a decyl group, a lauryl machine, etc. are mentioned, and a pentyl machine, a hexyl machine, a heptyl machine, and an octyl machine are desirable. Moreover, as an alkoxy group of carbon numbers 4-20, a butoxy machine, a pentyloxy machine, a hexyloxy machine, a heptyloxy machine, an octyloxy machine, a decyloxy machine, a lauryl oxy-basis, etc. are mentioned, and a pentyloxy machine, a hexyloxy machine, a heptyloxy machine, and an octyloxy machine are desirable. As an alkyl thio machine, a butyl thio machine, a pentyl thio machine, a hexyl thio machine, a heptyl thio machine, an octyl thio machine, a decyloxy machine, a laurylthio machine, etc. are mentioned, and a pentyl thio machine, a hexyl thio machine, a heptyl thio machine, and an octyl thio machine are desirable. As an aryl group, a phenyl group, a 4-C1 - C12 alkoxy phenyl group, 4-C1 - C12 alkylphenyl machine, 1-naphthyl group, 2-naphthyl group, etc. are illustrated. A phenoxy machine is illustrated as an aryloxy group. As a heterocyclic-compound machine, 2-thienyl group, 2-pyrrolyl machine, 2-furyl machine, 2-, 3-, or 4-pyridyl machine is illustrated. Although the number of these substituents differs from the molecular weight of this macromolecule fluorescent substance also by composition of a unit repeatedly, it is desirable that the viewpoint which obtains a soluble high macromolecule fluorescent substance to these substituents are one or more per molecular weight 600.

[0018] In addition, the macromolecule fluorescent substance used for the organic EL element of this invention may be randomness, a block, or a graft copolymer, and may be the macromolecule which has those middle-structures, for example, the random copolymer which wore block nature. From a viewpoint which obtains the high macromolecule fluorescent substance of the quantum yield of fluorescence, a random copolymer, and the block or graft copolymer which wore block nature is more desirable than a perfect random copolymer. Moreover, since the organic EL element of this invention uses luminescence from a thin film, that in which this macromolecule fluorescent substance has fluorescence by the solid state is used.

[0019] As a good solvent to this macromolecule fluorescent substance, chloroform, a methylene chloride, a dichloroethane, a tetrahydrofuran, toluene, a xylene, etc. are illustrated. although based also on the structure and molecular weight of a macromolecule fluorescent substance -- usually -- these solvents -- more than 0.1wt% -- it can be made to dissolve

[0020] The molecular weight of the macromolecule fluorescent substance in this invention is 103-107 in polystyrene conversion, and those polymerization degree changes also with repeat structure or its rate. general [from the point of membrane formation nature] -- the total number of repeat structure -- desirable -- 4-10000 -- further -- desirable -- 5-3000 -- it is 10-2000 especially preferably

[0021] When forming membranes from a solution by using the macromolecule fluorescent substance of such organic-solvent fusibility, in the case of organic EL-element creation, when [which mentions this solution later that what is necessary is just for the dryness after an application to remove a solvent] charge transportation material and luminescent material are mixed further, the same technique can be applied, and it is very advantageous to it on manufacture.

[0022] Although not limited especially as a synthesis method of the macromolecule fluorescent substance used for the organic EL element of this invention, the Wittig reaction from the diphosphonium salt obtained from the dialdehyde compound which two aldehyde groups combined with the arylene machine, the compound which two halogenation methyl groups combined with the arylene machine, and triphenyl phosphine, for example is illustrated. Moreover, as other synthesis methods, the

dehydrohalogenation method from the compound which two halogenation methyl groups combined with the arylene machine is illustrated. Furthermore, the sulfonium salinity solution method which obtains this macromolecule fluorescent substance from the intermediate field obtained by carrying out the polymerization of the sulfonium salt of the compound which two halogenation methyl groups combined with the arylene machine with alkali with heat treatment is illustrated. Since the structure of the repeat unit included in the macromolecule fluorescent substance generated by adding as a monomer the compound which has frames other than an arylene machine also in which synthesis method, and changing the abundance is changeable, you may adjust, teach and copolymerize so that the repeat unit shown by the general formula (1) may become more than 50 mol %. The method by the Wittig reaction is [among these] desirable in respect of control of a reaction, or yield.

[0023] The synthesis method of the arylene vinylene system copolymer which is one example of the macromolecule fluorescent substance used for the organic EL element of this invention is explained still more concretely. When obtaining a macromolecule fluorescent substance by the Wittig reaction for example, -- first -- a screw (halogenation methyl) compound -- more specifically 2 and 5-dioctyl oxy--p-KISHIRI range bromide For example, the inside of an N.N-dimethylformamide solvent, It is made to react with triphenyl phosphine and phosphonium salt is compounded. on this, a dialdehyde compound, and a twist concrete target For example, the macromolecule fluorescent substance containing a phenylenevinylene machine and a 2 and 5-dioctyl oxy--p-phenylenevinylene machine is obtained by the Wittig reaction which makes a terephthal aldehyde condense for example, among ethyl alcohol using lithium ethoxide. In order to obtain a copolymer, you may make two or more kinds of diphosphonium salts, and/or two or more kinds of dialdehyde compounds react at this time.

[0024] Since the purity affects a luminescence property when using these macromolecule fluorescent substances as a luminescent material of an organic EL element, it is desirable after composition to carry out purification processing of judgment by reprecipitation refining and the chromatograph etc.

[0025] Next, the protective layer used for the organic EL element of this invention is explained. It is isolated so that the organic EL element of this invention may be inserted with two transparent or translucent boards or film the interval from an anode plate front face or whose interval from a cathode surface is 100 micrometers or more 1mm or less preferably 1 micrometers or more 2mm or less and may not contact the open air. It is covered with the covering object which specifically consists of a joint which joins two transparent or translucent boards, a film and these two boards, or a film as this element, and the example isolated so that the open air may not be contacted is given. Since a crack may occur for an element when this element is directly joined to the both sides of two boards or a film, it is not desirable. Since glass, a polyethylene terephthalate (PET), a dampproof film, etc. are mentioned and glass and a dampproof film cannot penetrate the moisture in air, and oxygen easily as a material used for this board or a film, it is desirable.

[0026] The space between this element, this board, or a film, for example, the space between this element and this covering object, is filled with the inactive gas. As an inactive gas, nitrogen, an argon, helium, or a carbon dioxide is desirable, and an argon and nitrogen are still more desirable. In addition, the moisture content in an inactive gas has desirable 1000 ppm or less in order to prevent degradation of an element, and its 100 ppm or less are still more desirable.

[0027] About the structure of the organic EL element of this invention, the above-mentioned macromolecule fluorescent substance is used into the luminous layer which at least one side prepares in inter-electrode [of a transparent or translucent couple]. as a protective layer Since it is isolated so that the open air may not be contacted in this organic EL element, if it is covered with two transparent or translucent boards or film separated in 1-micrometer or more space 2mm or less filled with the inactive gas, there will be especially no limit and well-known structure will be adopted. For example, the thing of structure which has the electrode of a couple to both sides of the luminous layer which consists of this macromolecule fluorescent substance, or the luminous layer which consists of mixture of this macromolecule fluorescent substance and charge transportation material (the general term of electronic transportation material and electron hole transportation material is meant), What carried out the laminating of the electron hole transporting bed which contains electron hole transportation material

between a luminous layer and an anode plate, What carried out the laminating of the electronic transporting bed which carries out the laminating of what carried out the laminating of the electronic transporting bed which contains electronic transportation material between a luminous layer and cathode, and the electron hole transporting bed which contains electron hole transportation material between a luminous layer and an anode plate further, and contains electronic transportation material between a luminous layer and cathode is illustrated. Moreover, about a luminous layer or a charge transporting bed, the case of one layer, and when combining two or more layers, it is contained in this invention. Furthermore, you may carry out mixed use of the luminescent material stated to a luminous layer at the following for example, other than this macromolecule fluorescent substance. Moreover, it can also consider as the layer which made the high molecular compound distribute this macromolecule fluorescent substance and/or charge transportation material.

[0028] the charge transportation material used with the macromolecule fluorescent substance of this invention -- that is Although a thing well-known as electronic transportation material or an electron hole transportation material can be used and it is not limited especially As an electron hole transportation material, a pyrazoline derivative, an arylamine derivative, a stilbene derivative, A triphenyl diamine derivative etc. as an electronic transportation material An OKISA diazole derivative, An anthraquinodimethan and its derivative, a benzoquinone, and its derivative, A naphthoquinone and its derivative, anthraquinone, and its derivative, a tetracyano ANSURA quinodimethan and its derivative, and full -- me -- non, the metal complex of a derivative, diphenyl dicyano ethylene and its derivative, a diphenylquinone derivative, 8-hydroxyquinoline, and its derivative etc. is illustrated

[0029] Specifically, what is indicated by JP,63-70257,A, a 63-175860 official report, JP,2-135359,A, 2-135361, 2-209988, 3-37992, and the 3-152184 official report is illustrated. As an electron hole transportation material, as a triphenyl diamine derivative and an electronic transportation material, an OKISA diazole derivative, A benzoquinone and its derivative, anthraquinone, and its derivative, The metal complex of 8-hydroxyquinoline and its derivative is desirable. especially As an electron hole transportation material, a 4 and 4'-screw (N(3-methylphenyl)-N-phenylamino) biphenyl, as electronic transportation material -- 2-(4-biphenyl)-5-(4-t-butylphenyl)- 1, 3, 4-OKISA diazole, a benzoquinone, anthraquinone, and tris (eight quinolinol) aluminum are desirable What is necessary is just to use simultaneously the compound of electronic transportability, the compound of electron hole transportability, or both among these. These may be used independently, and may mix and use two or more kinds.

[0030] What is necessary is just to form a charge transporting bed using such charge transportation material, when preparing a charge transporting bed further between a luminous layer and an electrode. Moreover, what is necessary is just to decide suitably in consideration of them in the range which does not check sufficient membrane formation nature and a luminescence property, since the amount of the charge transportation material used changes with kinds of compound to be used etc. when mixing and using charge transportation material for a luminous layer. Usually, it is 1 - 40 % of the weight to luminescent material, and is 2 - 30 % of the weight still more preferably.

[0031] Although not limited especially as a well-known luminescent material which can be used with the macromolecule fluorescent substance in this invention, coloring matter, such as a naphthalene derivative, an anthracene and its derivative, a perylene and its derivative, a poly methine system, a xanthene system, a coumarin system, and a cyanine system, 8-hydroxyquinoline and the metal complex of the derivative, an aromatic amine, a tetrapod phenyl cyclopentadiene and its derivative, a tetrapod phenyl butadiene, its derivative, etc. can be used, for example. Specifically, what is indicated by JP,57-51781,A and the 59-194393 official report is usable.

[0032] Next, the typical production method of an organic EL element using the luminescent material of this invention is described based on drawing 1 . In addition, about the pattern of an anode plate and cathode, since a well-known pattern can be used, the detail of the pattern is omitted by drawing 1 . Moreover, in drawing 1 , when one sheet of two transparent or translucent boards or a film serves as the substrate of an anode plate, it corresponds. What formed the transparent or translucent electrode as an anode plate 4 on transparent or translucent a board or films 1, such as glass and transparent plastics, is

used. As a material of an anode plate 4, a conductive metallic-oxide film, a translucent metal thin film, etc. are used. The films (NESA etc.) created using the electrically conductive glass which specifically consists of indium tin oxide (ITO), tin oxide, etc., gold, platinum, silver, copper, etc. are used. As the production method, a vacuum deposition method, the sputtering method, plating, etc. are used. The thing same also as cathode 8 is used.

[0033] On this anode plate 4, the luminous layer 6 which contains the above-mentioned macromolecule fluorescent substance or this macromolecule fluorescent substance, and charge transportation material as a luminescent material is formed. Although the applying methods, such as the spin coating method, the casting method, a dipping method, the bar coat method, and the roll coat method, are illustrated as the formation method using the melting liquid, solution, or mixed liquor of these material, especially the thing to form using a solution or mixed liquor is desirable.

[0034] 1nm - 1 micrometer is 2nm - 500nm still more preferably preferably as thickness of a luminous layer 6. In order to raise current density and to gather luminous efficiency, the range of 5-200nm is desirable. In addition, when a luminous layer 6 is thin-film-ized by the applying method, in order to remove a solvent, it is desirable to carry out stoving of the 30-300 degrees C at the temperature of 60-200 degrees C preferably under reduced pressure or an inert atmosphere after luminous layer formation.

[0035] When carrying out the laminating of the electron hole transporting bed 5 to the bottom of this luminous layer 6, before forming a luminous layer 6 by the above-mentioned membrane formation method (when shown in drawing 1), it is desirable to form the electron hole transporting bed 5. Although not limited, especially as the membrane formation method of the electron hole transporting bed 5 The vacuum deposition method from a powder state, Or the spin coating method after melting in a solution, the casting method, The applying methods, such as a dipping method, the bar coat method, and the roll coat method, or the spin coating method after mixing a high molecular compound and charge transportation material in the state of a solution state or melting and making it distribute, The applying methods, such as the casting method, a dipping method, the bar coat method, and the roll coat method, can be used.

[0036] Especially as a high molecular compound to mix, although not limited, what has the absorption desirable what does not check charge transportation to a degree very much and not strong to the light is used suitably. For example, poly (N-vinylcarbazole), the poly aniline and its derivative, the poly thiophene and its derivative, poly (p-phenylenevinylene) and its derivative, poly (2, 5-thienylene vinylene) and its derivative, a polycarbonate, a polyacrylate, poly methyl acrylate, a polymethylmethacrylate, polystyrene, a polyvinyl chloride, a polysiloxane, etc. are illustrated. When using a high molecular compound in that membranes can be formed easily, it is desirable to use the applying method.

[0037] Although thickness which a pinhole does not generate at least is required for it, if the thickness of the electron hole transporting bed 5 is not much thick, resistance of an element increases and its high driver voltage is not needed and desirable. Therefore, 1nm - 1 micrometer of 2nm - 500nm of thickness of a charge transporting bed is 5-200nm especially preferably still more preferably preferably.

[0038] Moreover, when carrying out the laminating of the electronic transporting bed 7 further on this luminous layer, after forming a luminous layer 6 by the above-mentioned membrane formation method (when shown in drawing 1), it is desirable to form the electronic transporting bed 7 on it.

[0039] Although not limited, especially as the membrane formation method of the electronic transporting bed 7 The vacuum deposition method from a powder state, Or the spin coating method after melting in a solution, the casting method, The applying methods, such as a dipping method, the bar coat method, and the roll coat method, or the spin coating method after mixing a high molecular compound and charge transportation material in the state of a solution state or melting and making it distribute, The applying methods, such as the casting method, a dipping method, the bar coat method, and the roll coat method, can be used.

[0040] Especially as a high molecular compound to mix, although not limited, what has the absorption desirable what does not check charge transportation to a degree very much and not strong to the light is used suitably. For example, poly (N-vinylcarbazole), the poly aniline and its derivative, the poly

thiophene and its derivative, poly (p-phenylenevinylene) and its derivative, poly (2, 5-thienylene vinylene) and its derivative, a polycarbonate, a polyacrylate, poly methyl acrylate, a polymethylmethacrylate, polystyrene, a polyvinyl chloride, a polysiloxane, etc. are illustrated. When using a high molecular compound in that membranes can be formed easily, it is desirable to use the applying method. Although thickness which a pinhole does not generate at least is required for it, if the thickness of the electronic transporting bed 7 is not much thick, resistance of an element increases and its high driver voltage is not needed and desirable. Therefore, 1nm - 1 micrometer of 2nm - 500nm of thickness of a charge transporting bed is 5-200nm especially preferably still more preferably preferably. [0041] Subsequently, cathode 8 is formed on a luminous layer 6 or the electronic transporting bed 7. This cathode 8 turns into electron-injection cathode. Especially as the material, although not limited, a small material of ionization energy is desirable. For example, aluminum, an indium, magnesium, calcium, a lithium, a magnesium-silver alloy, a magnesium-indium alloy, a magnesium-indium alloy, a lithium-aluminium alloy, a lithium-silver alloy, a lithium-indium alloy, or a graphite thin film is used. A vacuum deposition method, the sputtering method, etc. are used as the production method of cathode. [0042] Next, one example of the manufacture method of the protective layer of the organic EL element in this invention is explained based on drawing 1 . By performing the following operations in an inactive gas, the space between this organic EL element, a transparent or translucent board, or a film, i.e., the space between this organic EL element and a covering object, is filled with the inactive gas 9. First, the 1-micrometer or more spacer 3 2mm or less is placed on a transparent or translucent board or a film 1 (it serves as a substrate.), and transparent or translucent another board or another film 10 is carried from this so that the organic electroluminescent element produced on the board transparent as mentioned above or translucent or the film 1 (it serves as a substrate.) may be surrounded. Next, a joint with a spacer 3, each two transparent or translucent boards, or a film is joined with an optical hardening type or the heat-hardened type adhesives 2, light-harden, or this joint is made to heat-harden, and two transparent or translucent boards or a film is joined. Thereby, an organic EL element is intercepted with the open air.

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OPERATION

[Function] Since the melting point and the decomposition temperature use comparatively high polymeric materials, it is thermally stable that the organic EL element of this invention is excellent, and it is because a luminous layer can be easily formed by the applying method. For this reason, high brightness and the organic EL element of high luminous efficiency can be produced very easily. Furthermore, it is thought that it is effective in reinforcement being possible since especially the endurance of cathode is high, and suppressing generation of a dark spot by operation of the protective layer used by this invention.

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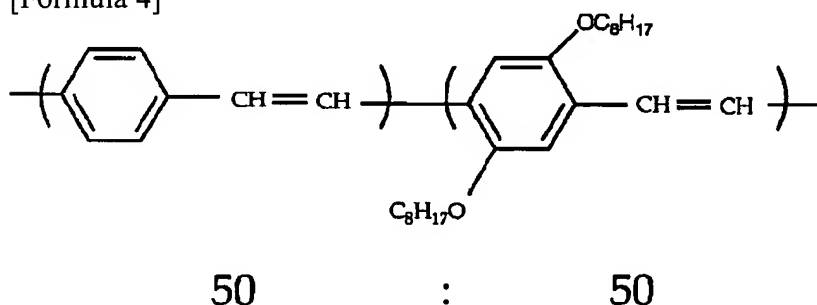
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EXAMPLE

[Example] Hereafter, although the example of this invention is shown, this invention is not limited to these. Here, about number average molecular weight, the number average molecular weight of polystyrene conversion was calculated by the gel permeation chromatography (GPC) by using chloroform as a solvent.

Example 1 <composition of macromolecule fluorescent substance 1> 2 and 5-dioctyl oxy--p-KISHIRI range bromide was made to react with the inside of an N.N-dimethylformamide solvent, and triphenyl phosphine, and phosphonium salt was compounded. The obtained phosphonium salt 47.75 weight section and the terephthal aldehyde 6.7 weight section were dissolved in ethyl alcohol. The ethyl alcohol solution containing the lithium ethoxide of the 5.8 weight sections was dropped at the ethyl alcohol solution of phosphonium salt and a dialdehyde, and the polymerization was carried out at the room temperature for 3 hours. After leaving it at an overnight room temperature, precipitation was carried out the ** exception, with ethyl alcohol, the dissolution was added to chloroform after washing, ethanol was added to this, and reprecipitation generation was carried out. Reduced pressure drying of this was carried out, and the polymer 8.0 weight section was obtained. This is called macromolecule fluorescent substance 1. The repeat unit and mole ratio of the macromolecule fluorescent substance 1 calculated from the preparation ratio of a monomer are shown below.

[Formula 4]



Here, two repeat units are combined by turns: the number average molecular weight of polystyrene conversion of this macromolecule fluorescent substance 1 -- 1.0x10⁴ it was . About the structure of this macromolecule fluorescent substance 1, it checked by the infrared absorption spectrum and NMR. [0045] By creation of an element, and <evaluation> sputtering, the 1.0wt% chloroform solution of a polyvinyl carbazole was used for the glass substrate which attached the ITO film by the thickness of 40nm, and membranes were formed by the thickness of 50nm by dipping. Furthermore, membranes were formed by the thickness of 50nm with the spin coat using the 1.0wt% toluene solution of the macromolecule fluorescent substance 1. Furthermore, after drying this at 150 degrees C under reduced pressure for 1 hour, 35nm (Alq3) of tris (eight quinolinol) aluminum was deposited bynm [0.1-0.2 //s / in speed] as an electronic transporting bed. 40nm vacuum evaporation of the lithium-aluminium alloy (lithium concentration : 1wt%) was carried out as 1st metal layer of cathode on it, and the organic EL element was produced. All the degree of vacuums at the time of vacuum evaporation were 8x10 to 6 or

less Torr. After electrode production, the spacer of 1mm glass was put on the circumference of the organic EL element produced on the transparent substrate in nitrogen-gas-atmosphere, the glass plate was carried from on this, and the organic EL-element protective layer was produced by pasting up a substrate and this glass plate for the spacer section using optical hardening type adhesives. When voltage 12.5V are impressed to this element, the current of 2 flows the current density of 32.1mA/cm, and it is brightness 1892 cd/m². Yellow-green EL luminescence was observed. The luminous efficiency at this time was 5.9 cd/A. Brightness was proportional to current density mostly. Moreover, EL peak wavelength was 540nm, simultaneously coincidence is carried out with the fluorescence peak wavelength of the thin film of the macromolecule fluorescent substance 1, and EL luminescence [fluorescent substance / macromolecule / 1] was checked. When the low-battery drive of this element was carried out by 10V after preservation for five days in air, there was little generating of a dark spot and the area for a non-light-emitting part was 10% or less.

[0046] The element was created by the same method as an example 1 except not using the protective layer of an example of comparison 1 organic EL element. When voltage 12.5V were impressed to this element, it is 2 the current density of 32.1mA/cm. Current flows and it is brightness 1892 cd/m². Yellow-green EL luminescence was observed. The luminous efficiency at this time was 5.9 cd/A. Brightness was proportional to current density mostly. Moreover, EL peak wavelength was 540nm, simultaneously coincidence is carried out with the fluorescence peak wavelength of the thin film of the macromolecule fluorescent substance 1, and EL luminescence [fluorescent substance / macromolecule / 1] was checked. When the low-battery drive of this element was carried out by 10V after preservation for five days in air, there was much generating of a dark spot and the area for a non-light-emitting part was about about 50%.

[0047] Thus, rather than the organic EL element of the example 1 of comparison which is not covered by the glass plate of two sheets separated in the 1mm space filled with the inactive gas, the organic EL element covered by the glass plate of two sheets separated in the 1mm space where the organic EL element of an example 1 was filled with the inactive gas had little generating of a dark spot, and showed the preservation property of the outstanding luminescence display grace.

[Translation done.]